

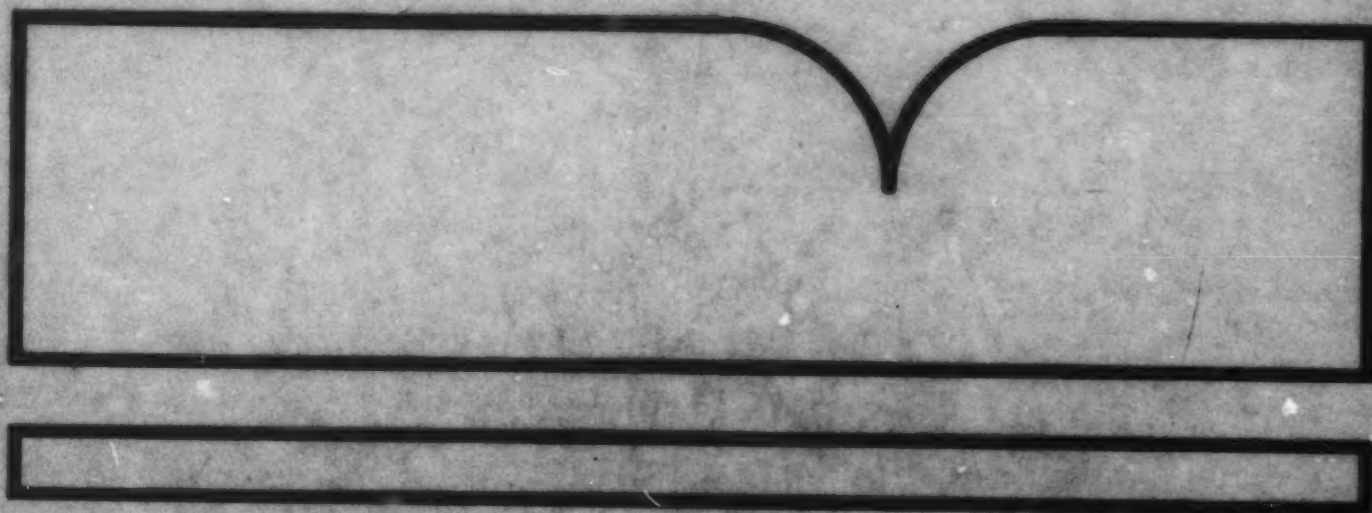
**Automotive Crankcase Oil: Detection in a
Coastal Wetlands Environment**

Hunter Coll., New York

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Mar 81



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**AUTOMOTIVE CRANKCASE OIL:
DETECTION IN A COASTAL WETLANDS ENVIRONMENT**

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

When energy and material resources are extracted, processed, converted, and used, the related pollutorial impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Municipal Environmental Research Laboratory-Cincinnati (MERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It identifies the presence of waste automotive petroleum hydrocarbons in the treated wastewater effluents of water pollution control facilities (WPCF's) which discharge into Jamaica Bay, New York. It also identifies and quantitates petroleum derived benthic organisms (bivalves). This report further documents the application of a novel technique using fluorescence spectroscopy for identification of waste automotive petroleum hydrocarbons in effluents. This report will be of interest to those individuals involved in routine monitoring of the environment, damage assessment, law enforcement, and industrial wastewater research. Further information about this report is available from the Oil and Hazardous Materials Spills Branch, MERL-Ci, Edison, New Jersey 08817.

Francis T. Mayo, Director
Municipal Environmental Research
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ABSTRACT

Samples from four sewage treatment facilities which discharge into Jamaica Bay, New York, were analyzed for the presence of waste automotive oil products. UV-fluorescence spectroscopic techniques were utilized to qualitatively identify waste petroleum hydrocarbons in effluents of water pollution control plants by comparison of sample profiles to profiles generated by standard reference oils. Within the Bay, surface waters and a benthic bivalve (*Mya arenaria* L.) were also analyzed for petroleum hydrocarbons using fluorescence techniques, and gas chromatography. GC-Mass spectroscopy was used to further aid in establishing the presence of petroleum hydrocarbons in the bivalves. Synchronized excitation fluorescence spectroscopy was used in this investigation to confirm the presence of waste automobile oil in the environmental samples. Results strongly indicated the presence of hydrocarbons associated with waste automotive petroleum products in most of the extracts of effluent samples, surface water samples and bivalves.

This work covers the period September 1973 to April 1974, and was completed in May 1974. Professor Tanacredi is Adjunct Assistant Professor of Human Ecology at the Institute of Health Sciences, Department of Environmental Health Science, Hunter College, City University of New York. At the time of this project, Professor Tanacredi was on a Department of Health, Education and Welfare Fellowship Grant. Project support in part was provided by U.S. Environmental Protection Agency-Edison, New Jersey and Hunter College, C.U.N.Y.

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ABBREVIATIONS AND SYMBOLS

WPCF	--Water Pollution Control Facilities
SCOT	--support coated open tubular column
ID	--inside diameter
WCCO	--waste crankcase oil
PNA	--polynuclear aromatics
UEP	--unresolved envelope portion
ul	--microliter
GC-MS	--gas chromatography-mass spectroscopy
FMP	--Fluorescence Maxima Profile
CCL ₄	--carbon tetrachloride
HPP ₄	--high pollution potential
LPP	--low pollution potential
HEM	--hexane extractable materials

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The specialized assistance afforded me throughout this study by Mr. M. Gruenfeld, Mr. U. Frank of the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and Dr. B. Dudenbostel of the Surveillance and Analysis Division, Region II, U.S. EPA, Edison, New Jersey was instrumental in the successful completion of this project.

The weekly collection of the final effluents from the major Water Pollution Control Facilities emptying into Jamaica Bay could not have been possible without the cooperation of the Bureau of Water Resources, City of New York and its then commissioner, Mr. Martin Lang.

Finally, I would like to acknowledge the consistent aid and support provided by Dr. George J. Kupchik, Program Director of the Department of Environmental Health Sciences, Hunter College of the City University of New York, whose insight into the relevancy of this project made it possible.

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SECTION 1

INTRODUCTION

Recent years have shown our aquatic ecosystem to be an invariable disposal ground for an ever increasing number of waste products. Among this perplexing myriad of disposables is a considerable quantity of waste petroleum. As the world demand for petroleum products mushrooms each year, the probability of greater concentrations of specific hazardous materials such as petroleum derived hydrocarbons entering the aquatic environment will increase.

Even though petroleum products are subject to varied degrees of environmental degradative processes such as wind, wave and bacterial action, their continued disposal into the marine ecosystem makes it imperative to consider them in the same context as heavy metals and pesticides. Blumer had noted that early interpretations and investigations of the environmental effects of oil pollutants were based on subjective observations over relatively short periods of time. These data may now have questionable validity since it has been demonstrated^{2,3} that these oil products are persistent poisons resembling in their longevity DDT, PCB's and other synthetic materials. The environmental persistence of these petroleum hydrocarbons has been well demonstrated. Petroleum hydrocarbons have persisted in offshore sediments years after significant quantities of fuel oil was spilled. Specific hydrocarbon incorporation in tissue has been exhibited⁵⁻⁷ in everything from the basking shark to species of marine algae.

According to U.S. Department of Commerce figures⁸, sales of new oils in the United States total about 2.5 billion gallons annually of which half goes to use in the automotive industry. The American Petroleum Institute has estimated⁹ that 68% of the automotive lubricating oils utilized leaves car engines as waste. Of this 850 million gallons, it is estimated¹⁰ that 200 to 400 million gallons is recycled annually, with only 100 million gallons actually being re-refined. Thus, between 450 and 650 million gallons of waste crankcase oil (WCCO) is subject to man's re-use or mis-use.

It has been estimated¹¹ that a substantial quantity of waste petroleum products, approaching 1,400 million gallons per year, is being lost to the environment, of which a substantial quantity is being indiscriminately dumped into our nation's municipal sewerage systems and their receiving waters. The origin of this oil can be from a variety of sources ranging from industrial wastes to the individual who changes the oil in his automobile and dumps the wasted crankcase oil into a nearby sewer. Apartment houses dumping tank bottom wastes from spent home heating fuels, garages, gas stations, bus depots, truck terminals, railroad yards and marinas whose vessels all require regular changes of lubricating oils, all generate

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substantial quantities of waste oils.

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Assuming that a significant quantity of this waste oil is being discarded into municipal sewerage systems of New York City, existing wastewater treatment technology will not prevent a major portion of this waste petroleum from getting into a receiving body of water. This assumption is based upon the facts that (a) most hydrocarbons are more resistant to degradation processes than other organic compounds commonly found in sewage¹², and (b) hydrocarbons are only removed by skimming and settling operations which disregard that portion of waste oil which is finely dispersed¹³. The effects of exposure to various petroleum hydrocarbons on a variety of marine organisms are well documented^{14,21}.

Only about 40% of the estimated 94 million gallons of automotive and industrial waste petroleum recorded annually in the New York City metropolitan area is being reprocessed; approximately 25 million gallons are actually being re-refined²². Now more than ever, with the continuing energy dilemma, it seems imperative to consider this waste not only as a potential detriment to the marine environment but also as a potential energy source.

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The analytical methods available for the identification and detection of oil products in the environment are varied and extensive²³⁻²⁵. However, no single method of analysis is a confirmation for the identification of a specific waste petroleum pollutant. Any or all of the methods utilized in this project⁹ may be considered as confirmative evidence for the detection of petroleum hydrocarbons. Specific pollutant identification can only be considered in the light of a multi-parameter approach²⁶. Accumulation of as convincing a group of evidence as is possible, aids in pinpointing the origin of these waste petroleum products. For these reasons UV-fluorescence spectroscopy and gas chromatography are to be the principal analytical tools utilized for the detection of waste automotive petroleum products in environmental samples. Mass spectroscopy will be utilized for the identification of some specific petroleum derived hydrocarbons in biological tissue of a marine bivalve.

The objective of this study was to determine whether automotive petroleum derived hydrocarbons were present in the wastewater final effluents emitted by water pollution control facilities discharging into Jamaica Bay, New York.

With the detection of a chronic addition of relatively low levels of waste petroleum hydrocarbons into the environment, the study examined (by identification and quantitation) whether these petroleum derived hydrocarbons disseminated through the Bay ecosystem. In addition, the petroleum derived hydrocarbon contents of the surface waters and the tissues of an intertidal bivalve (Mya arenaria L.) were analyzed.

Immediate effects of continuous additions into a marine ecosystem may not be as dramatic as a major oil spill, however, the final outcome could be more significant over an extended period of time and in the proper ecological conditions.

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CONCLUSIONS

The results of this study strongly suggest that appreciable quantities of hydrocarbons attributable to waste automotive crankcase oil were detected in treated wastewater effluents entering Jamaica Bay, New York.

The weekly occurrence of detectable quantities of petroleum hydrocarbons in WPCF effluents suggests that the discharge of these hydrocarbons should be considered as a chronic input of petroleum waste products into Jamaica Bay.

Significant quantities of detectable petroleum derived hydrocarbons are remaining in solution in the near-surface waters of the Bay.

Compounds isolated from tissue extracts of marine benthic organisms collected in the Bay appear to be attributable to the aromatic hydrocarbon portion of automotive petroleum products.

A continuing monitoring system for wastewaters within the New York metropolitan area should be established addressing petroleum derived hydrocarbons.

Increased efforts should be made to monitor levels of toxic hydrocarbons, particularly polynuclear aromatic compounds, in the Jamaica Bay ecosystem. Critical areas of the Bay sediments, water and key fauna should be analyzed to determine whether food web transfer, bioconcentration, or hazards to human health exist.

Research to identify and quantitate specific petroleum derived compounds, their sources and fate in the environment and biota should be conducted. This data should be compiled and a hydrocarbon modeling system should be established.

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PRIMER ON PETROLEUM CHEMISTRY

Products derived from crude petroleum are complex organic hydrocarbon compounds. Table 1 shows the more important of the simpler series for fuels and lubricants. The compounds in a homologous series have similar chemical properties, and there is a gradual change in physical properties as the molecular weight increases. The alkanes contain single bonds only, and straight chain alkanes are called n-paraffins. Additions of substituent groups, or the branching of side chains, results in a complex arrangement of isomeric compounds. In general, the boiling points and densities for the branched chain isomers are lower than the values for the corresponding normal isomer²⁷. The highly branched paraffins are desirable components in some petroleum products²⁸. High molecular weight normal paraffins are provided in lubricating oils so as to maintain a better viscosity state, while the extremely high molecular weight n-paraffins above C₄₀ are usually removed in dewaxing processes. The complex mixture of cycloparaffinic and aromatic compounds (mono and polyalkylated benzenes and polynuclear aromatics) with substituted and unsubstituted ring structures, are fundamentally found in petroleum products²⁹. The olefinic compounds are present in most refinery products such as the automotive lubricating oils³⁰.

TABLE 1. HOMOLOGOUS SERIES FOR PETROLEUM PRODUCTS

Name	Carbon formula	Characteristics
Alkanes (paraffins)	$C_n H_{2n+2}$	Open chain, saturated
Alkenes (olefins)	$C_n H_{2n}$	Open chain, one double bond
Cycloalkanes, cycloparaffins (naphthenes)	$C_n H_{2n}$	Cyclic, saturated
Cyclo-olefins	$C_n H_{2n-2}$	Cyclic, one double bond
Aromatics	$C_n H_{2n-6}$	Single or multiple ring structures

Thus, the principle aspect of petroleum chemistry is its complexity of composition, upon which unique detection parameters are based. It is due to this complexity that no two petroleum entities will exhibit identical identification characteristics thus aiding in their detection in the environment.

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PROJECT APPROACH

Any multiparameter oil pollution identification scheme will involve three basic tasks: (1) the collection of and preparation from a suspected polluted sample, a representative of a previously established standard; (2) measurement of specific identification parameters (qualitative or quantitative) on the sample; (3) and the comparison of the measured parameters with standards. As the state-of-the-art in oil pollutant analysis exists today, "active" or "passive" identification techniques encompass these tasks as the two basic approaches which may be utilized when one is concerned with the detection of petroleum wastes in the environment. An "active" tagging approach requires the addition of specific chemicals to standard oils. Once these petroleum products permeate the marine environment, one differentiates between the suspected origins of the oils by looking for these "tags". These "chemical tags" are usually unaffected by weathering and will readily lend themselves to analysis.

Petroleum products can only be described in general terms because they are such a complex mixture of various hydrocarbons, and a wide range of inorganic and organic compounds. Whitehead and Breger³¹ point out that in the complex structure of a lubricating oil "the compounds may be composed of a mixture of aromatic, cycloparaffinic and paraffinic structures, whose number of possible combinations becomes almost infinitely large..." It has been estimated³² that within some refined petroleum products such as the automotive lubricating oils, some hydrocarbons have molecular weights which reach as high as 6,000. A refined petroleum product is the end result of various purification and blending processes. To obtain the properties desired in automotive oils, refineries use as a starting material specific fractions from crude oils. Even with the desired fraction from the original crude, many automotive lubricating oils demand specific, high boiling point, high molecular weight additives. These long chain polymeric compounds aid in maintaining a proper viscosity-state when these oils are subjected to the wide temperature ranges today's various means of transportation may experience. The addition of "active" tags to various petroleum products in some instances may have definite advantages, as is the case if the origin of the oil is known prior to analysis of the polluted sample. However, when one considers all the possible individual sources of waste automotive lubricating oils, one realizes that such an approach would be impractical. One must also consider the fact that little is known concerning the effects of weathering of these chemical tags³³, or for that matter what effect subsequent by-products could have on the environment.

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Regardless of all the refining processes and tagging problems, petroleum products are unique enough to lend themselves to differentiation from other

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petrochemical entities by utilization of a "passive" tagging approach. This passive detection technique utilizes the inherent chemistry of the oil itself. For instance, the qualitative parameters established for instrumental analyses generate a fingerprint or profile of a WCCO. These fingerprints are such that upon observing them one may clearly differentiate the WCCO from other petroleum materials such as crude or fuel oil. Analysis of off-the-shelf petroleum products, a used crankcase oil and weathered oils will serve as "reference standards" to compare with environmental sample extracts (Table 2). Those particular portions of the standard fingerprints which remain stable under environmental conditions will serve as the parameters for instrument analysis. For example, WCCO has been characterized³⁴ by large quantities of 4- and 5-ring polynuclear aromatic (PNA) compounds. This is one reason why WCCO has been established³⁵ as one of the major contributors (450,000 metric tons per year) of hydrocarbons to our ocean waters. Evidence indicates³⁶ that compounds with carbon numbers of 20 or greater may act as tags due to the fact that more volatile paraffins (C₁₈ or below) readily weather by evaporation. The effect of weathering on the PNA portion of specific fuel oils under simulated, yet vigorous temperature conditions, indicated no significant changes in the fingerprinting scheme for the C₁₀ to C₃₆ compounds³⁷. Therefore, by the use of a passive - tagging approach to detect such unique petroleum hydrocarbon constituents as PNA's or specific paraffinic compounds which do not occur naturally in the marine environment, one can demonstrate their presence in sample extracts through the generation of characteristic analytical profiles.

TABLE 2. PETROLEUM PRODUCTS UTILIZED AS "REFERENCE STANDARDS"

Refined petroleum products

1. Warco Dexron Automotive Transmission Fluid
2. Fox Head Multi-Grade SAE 10W/30 Motor Oil
3. Castrol XLR SAE 20W/50 Motor Oil

Waste crankcase motor oil

1. WCCO from 1966 Buick; 6,000 miles

Fuel oils^a

1. No. 2 Fuel Oil
2. No. 4 Fuel Oil
3. No. 5 Fuel Oil

Crude oils (See Appendix B for chromatograms)

1. South Louisiana Crude Oil
2. Bachaquero Crude Oil
3. Kuwait Crude Oil
4. Nigerian Medium Crude
5. Skidka Crude Oil

^a These oils were On-Hand reference standards supplied and utilized for analyses by the Industrial Waste Treatment Research Laboratory, Edison, New Jersey, a division of the Environmental Protection Agency's National Environmental Research Center.

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SECTION 5

STUDY AREA

Geographically, Jamaica Bay is approximately six miles long and four miles wide and receives relatively little fresh water input. There are no major rivers or streams which empty into the bay, and the major source of fresh water (besides precipitation and run off) is derived from the water pollution control facilities (WPCF) emptying into it³⁸. The Bay's only connection with the sea is at the Rockaway Inlet (Figure 1).

Jamaica Bay and its drainage area amounts to approximately 52,000 acres and serves an estimated population of over 1,600,000³⁹. Within the Bay proper, there are a number of inlets which receive the bulk of the combined sewer overflow discharges after periods of precipitation, and a portion of the waste discharges from water pollution control facilities. The final effluents from some plants enter the Bay at specific outfall sites (Figure 2). Those inlets which still drain marshland are confined to the central portion of the Bay within the Jamaica Bay Wildlife Refuge.

Jamaica Bay is an ideal location for this particular study. The Bay's hydrology affords a long residence time for the treated or untreated effluents pouring into it. The daily tidal fluctuations (semi-diurnal with a period of 12.4 hours) involve approximately 31% of the total volume of the Bay⁴⁰, which should indicate a great deal of mixing and flushing occurring with such a water exchange. This is true of the Bay waters in that sufficient turbulence exists to create extensive mixing and prevention of stratification. The net exchange of Bay water with ocean water during a tidal cycle is relatively small. It has been estimated⁴¹ that the net daily flow out of the Bay from all peripheral inputs is equivalent to an estimated 1% of the volume of the Bay, whereas the diurnal tidal flux is approximately fifty times greater than this value. Nearly all the waters entering the Bay on flood tides are carried by the peripheral channels. On ebb tides, an equivalent quantity of water moves back through the channels and into Rockaway Inlet.

Samples were not collected from the waters in the back of Grassy Bay, since such samples may contain oil pollutants attributable to the JFK airport operations. Jet fuels and other aviation lubricants however, should not affect established detection parameters for waste automotive lubricating oils.

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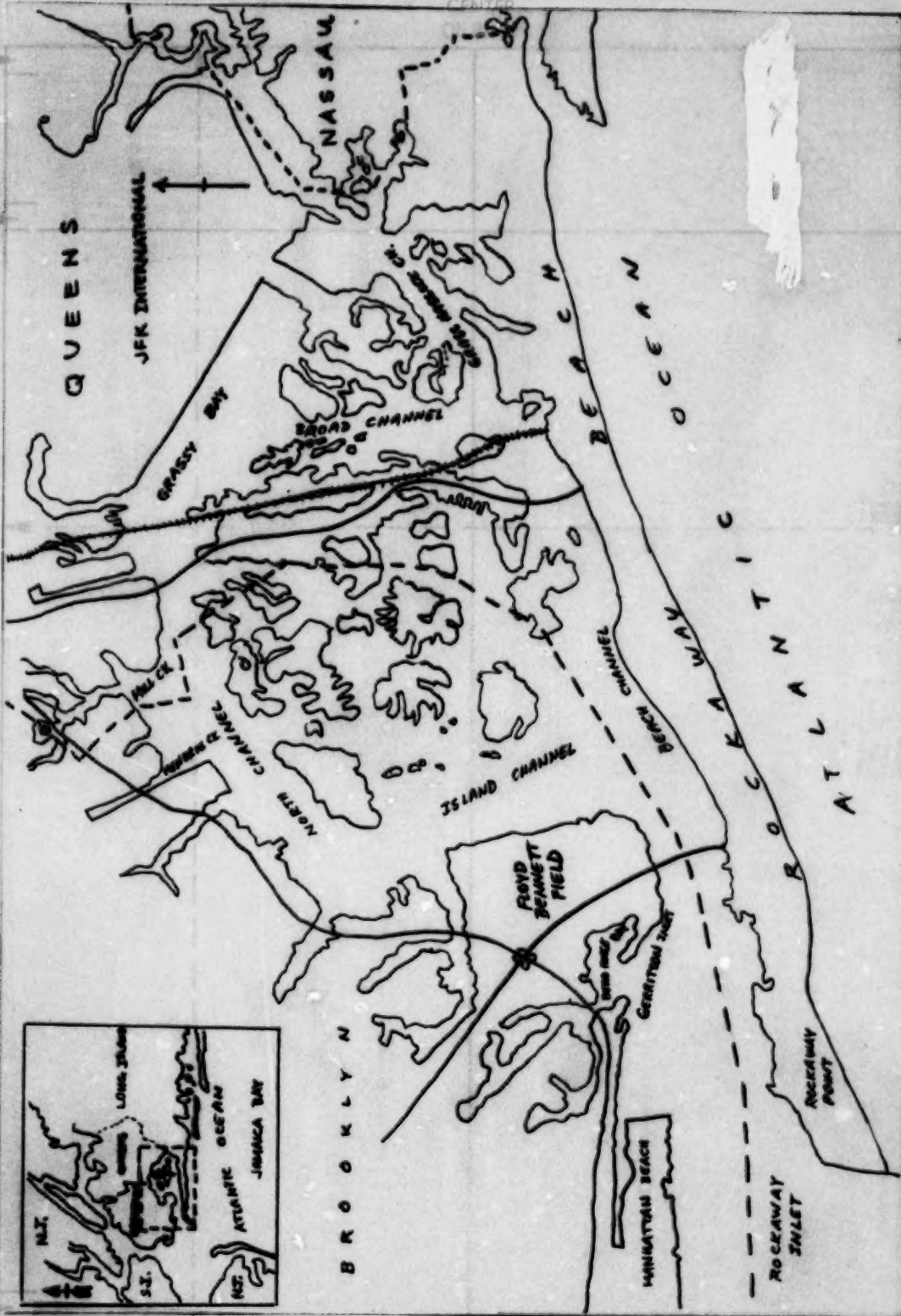
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Figure 1. Geographical map of Jamaica Bay.

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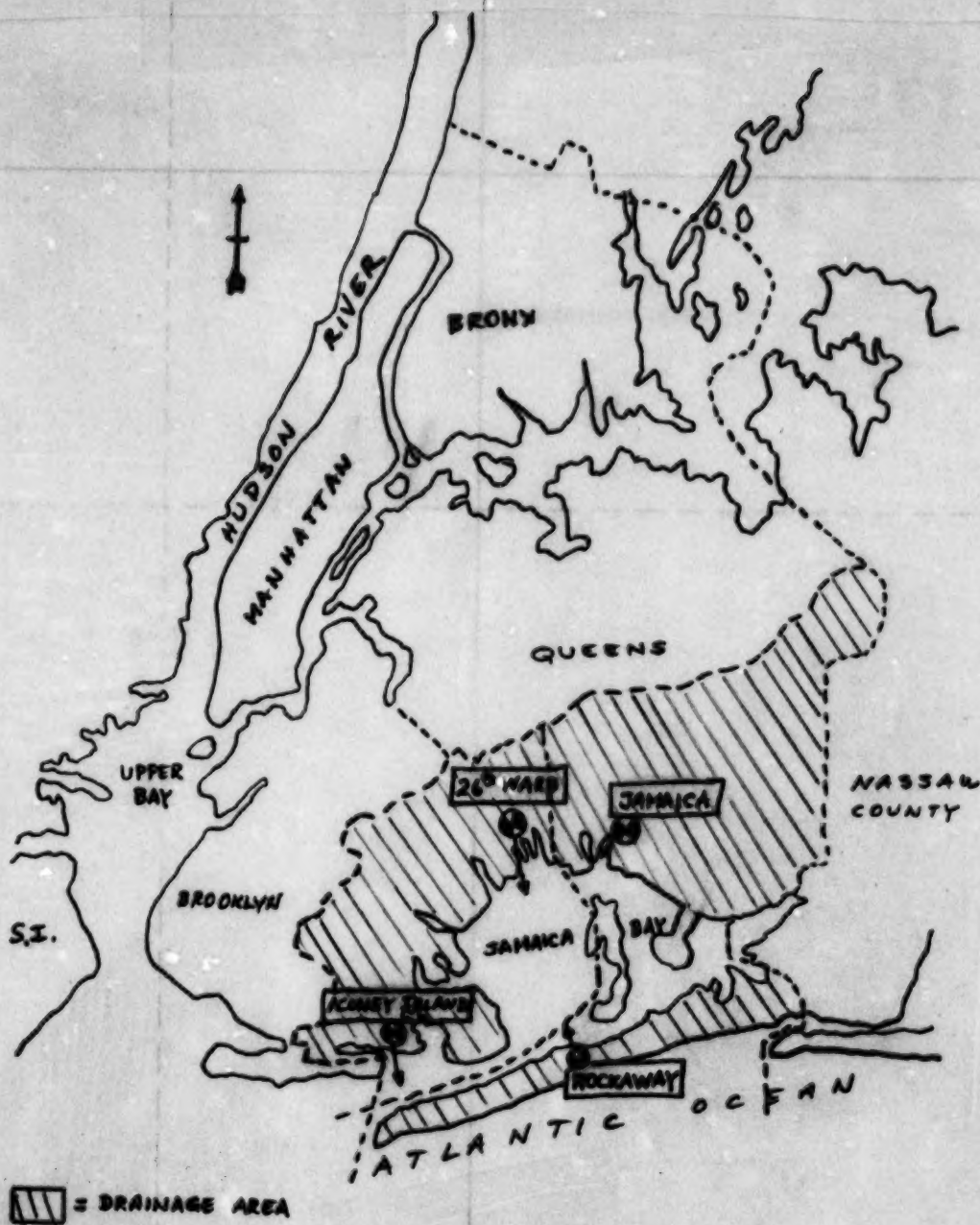


Figure 2. Jamaica Bay Water Pollution Control Facilities (WPCF)

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SECTION 6

SAMPLING SCHEME

The sampling operation consisted of three phases. The first phase involved the collection, on a weekly basis, of the final effluents of the major water pollution control facilities (WPCF) emptying into Jamaica Bay. Table 3 provides the total daily flows from all the plants pumping wastewater into the Bay during the period of this project along with their points of discharge⁴².

TABLE 3. DAILY FLOWS FROM WPCF

Facility	Flow (mgd)*	Point of discharge
NEW YORK CITY (1972 - 73)		
Coney Island	77	Rockaway Inlet
26th Ward	53	Hendrix Creek
Jamaica 9-1/8"	76	Grassy Bay
Rockaway	16	South Channel
Total:	222	
MILITARY INSTALLATIONS		
Floyd Bennett Field	0.3	
Fort Tilden	0.3	
NASSAU COUNTY		
Inwood	1.3	
Cedarhurst	1.0	

* 1977-1978 capacities total 360 mgd for NYC facilities.

From this table it can be observed that a relatively small quantity of treated effluents entering Jamaica Bay is derived from water pollution control facilities other than NYC plants. The WPCF's sampled were the Coney Island Plant located at Avenue Z and Knapp Street; the 26th Ward Plant located off Pennsylvania Avenue; the Jamaica Plant at the southwest corner of JFK International Airport; and the Rockaway Water Pollution Plant located along Beach Channel Drive in Rockaway Beach.

A combined sewer collection and treatment system such as we have in New York City is usually incapable of handling hydraulic loadings caused by storm generated flows. In many instances to avoid upsetting conventional treatment plant operations, such peak flows will be by-passed directly into a receiving body of water untreated. It was felt that after a particular storm period, a special effluent sample would be taken as representative of

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the combined sewer overflows as well as representative of a high potential oil content. Waste crankcase oil (WCCO) that has been dumped into a municipal sewer would remain within the system until rain waters caused this accumulation to be washed-out with overflows. In many instances large stocks of waste petroleum will be dumped sporadically by larger establishments. These larger quantities of waste oils have been observed by WPCF personnel as large "oil-sticks" or as "globules" which will usually go through WPCF's undetected and for the most part untreated. On the average, secondary treatment, that is skimming of surface layers and settling-out solid particles upon which oil adheres, will remove 48 to 96 per cent of the total hydrocarbons. Thus, even under normal situations, after some treatment, an average of 10 to 50 per cent of the total hydrocarbons found in sewage will be passed into a receiving body of water.

Ideally, once a treatment plant experiences a hydraulic rise in flow after a period of precipitation, a special sample should be taken as representative of an elevated level of waste petroleum products in the combined sewer overflow. Special sample collection without the serious interruption of normal plant operations, was unattainable for this project. The possibility of contamination was high for the special samples due to a regular turnover of individuals responsible for its collection. It was determined however, by the consistency of detectable oil pollutants found in the treated effluents, that for this project there was no need for such an integrated sampling scheme. Any subsequent quantitative work concerned with oil in wastewater effluents will require an extensive automatic sampling system for the precision monitoring of stormsewer overflows.

The second phase of the sampling scheme required the assistance of the Environmental Protection Agency's research vessel Clean Waters to take surface-water samples. Seven sites were selected; five within the Bay, one within the Rockaway Inlet and one off Breezy Point in the Atlantic Ocean (Figure 3). Two of these sites were regularly monitored by New York City's Bureau of Water Resources during the same months, while the other five sites had been previously sampled by the Federal Environmental Protection Agency's Region II, Surveillance and Analysis Division, located in Edison, New Jersey (Table 4). Samples were taken at a depth of 2 feet below the surface with a Kemmerer grab water sampler at all seven sites. Water samples were placed in 980 ml wide-mouth, glass Mason jars with teflon-lined caps. Since no refrigeration space was available for the samples aboard the ship, 5 ml of 1:1 concentration sulfuric acid and 20 ml carbon tetrachloride (CCl_4) were added to each sample collection so as to retard bacterial degradation of hydrocarbons. Samples were kept in ice until returned to laboratories where they were immediately refrigerated until extraction and analysis. The time period between collection of samples and extraction never exceeded 48 hours.

The third and final phase of the sampling operation required the collection of an estuarine benthic organism, Mya arenaria L., at sites felt to be representatives of (a) a high pollution potential (HPP) and, (b) a low pollution (LPP) for waste automotive petroleum wastes. It would be ideal to have access, for control purpose in this project, organisms reared in an environment free from contamination. However, when dealing with marine organisms directly from the ocean or coastal environment, especially from an estuarine

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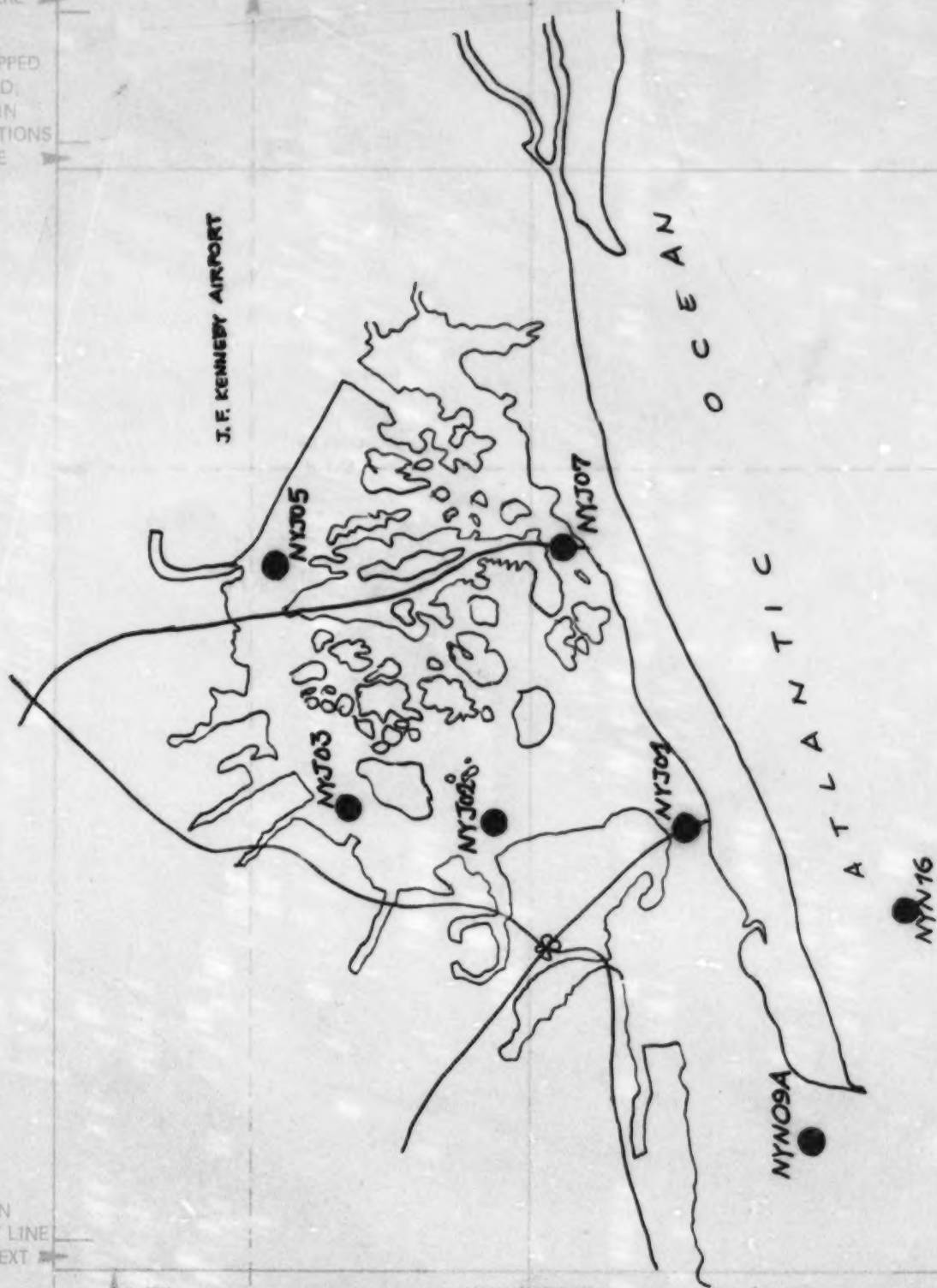


Figure 3. Surface-water sampling sites in Jamaica Bay.

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TABLE 4. LOCATION OF SURFACE SAMPLES TAKEN IN JAMAICA BAY

Sample station	Latitude	Longitude	Approximate site
NYN16	40.31.44	73.56.45	Atlantic Ocean
NYN09A	40.33.43	73.56.45	Off Rockaway Point
NYJ01*	40.34.22	73.53.05	Marine Parkway Bridge
NYJ02*	40.36.27	73.53.11	Floyd Bennett Field
NYJ03*	40.37.33	73.53.03	Canarsie Pier
NYJ05*	40.35.45	73.48.41	IND Train Tressel
NYJ07*	40.38.43	73.49.16	Broad Channel

* entered as EPA stations; latitude and longitude from EPA directory print-out.

area, there is no certainty of freedom from petrochemical contamination⁴⁵. Figure 4 indicates locations of organism samples collected in October (Mya I) and in December (Mya II and Mya III). At each site a total of 15 clams, ranging in size from 1.0 to 4.0 cm were collected and placed in a glass de-canter. The clams were shucked within one hour after collection and allowed to drain so that only body tissue and internal fluids would be used for extraction purposes. Each sample was placed in aluminum foil and immediately frozen until extraction and analysis.

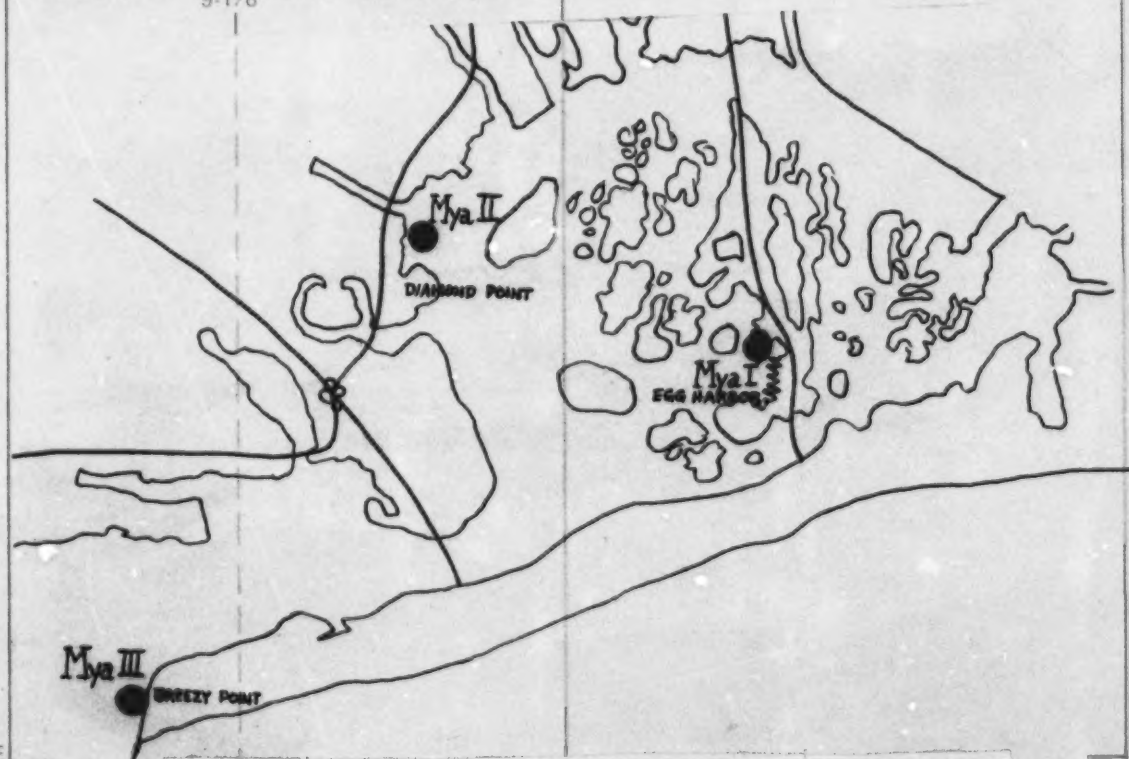


Figure 4. Benthic organism sampling sites in Jamaica Bay.

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SECTION 7

PROCEDURES FOR SAMPLE PREPARATION

SEWAGE TREATMENT PLANT EFFLUENTS

The quantity of extractable hydrocarbons in each final effluent sample was determined by utilizing an infrared (IR) method for the quantification of total hydrocarbons⁴⁶.

The samples were collected from the final contact tanks of each of the WPCF's sampled. Samples were taken in 980 ml, wide-mouth, glass bottles, each with a teflon-lined cap. The bottles were washed with a detergent (Surgical Instrument and Laboratory Glassware Detergent, Octagon Process Inc., Edgewater, N.J.) which has been reported⁴⁷ not to have any interfering residue on inner-glass surfaces. Each bottle was oven-dried at 120°C to ensure removal of any possible contaminants. The extent of contamination was determined by solvent washing bottles with 50 ml of carbon tetrachloride (CCL₄) and measuring solvent absorbance by IR in 10 mm cells. In all instances the resulting absorbance was negligible, and in no case did the absorbance exceed 0.01. Each sewage treatment facility received a sampling procedure. All samples from WPCF's were taken at 2:00 PM by plant personnel. All samples were refrigerated throughout the storage and transfer period prior to analysis. Five milliliters of 1:1 H₂SO₄ was added to each sample directly after pick-up at each plant to retard bacterial degradation of hydrocarbons.

Laboratory Procedure

The following procedure was carried out on each of the sewage effluent samples:

- (1) Quantitatively transfer sample to a 2 liter separatory funnel.
- (2) Rinse sample bottle with 25 ml of CCL₄ and add to separatory funnel.
- (3) Add 5 g sodium chloride and allow time for its going into solution.
- (4) Shake vigorously for one minute and allow 5-10 minutes for the phases to separate. (Usually a water/CCL₄ emulsion occurs, so that good separation should be attained before drainage of solvent layer. Try to prevent water from getting into tared beaker during sample extract collection.)
- (5) Check for acidity; sample acidity should be below pH3. If necessary adjust pH to 3 by addition of 1:1 solution of sulfuric acid.

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- (6) Prepare a one inch layer of anhydrous sodium sulfate over a small CCl_4 washed glass wool plug in a long stem funnel.
- (7) Drain the lower phase from the separatory funnel through the sodium sulfate into a tared 100 ml beaker. Avoid draining upper aqueous layer.
- (8) Perform three additional extractions with 25 ml portions of solvent using each portion to rinse the sample bottle. Allow the phases to separate and drain each bottom phase through sodium sulfate into a 100 ml beaker. Bring to volume with CCl_4 . This is the SAMPLE EXTRACT (As).
- (9) Scan the SAMPLE EXTRACT in the range 3200 cm^{-1} to 2600 cm^{-1} with an IR spectrophotometer, using CCl_4 in the reference beam. Select the appropriate path length cells (in this case 10mm cells) to obtain maximum absorbance NOT exceeding 0.9. Measure oil absorbance at 2930 cm^{-1} as the difference between the absorption band maximum and a "base-line" drawn tangent to the band minimum (see Figure 5).
- (10) After the measurement, return the extract having UNKNOWN identity to the original 100 ml beaker.
- (11) "Jet-air" evaporate off the solvent from the SAMPLE EXTRACT using a cool air stream ONLY, to dryness. Keep jet stream low to prevent possible aerosol formation. Perform this operation in a well ventilated hood. When no solvent remains record residue's weight in milligrams (Cr).
- (12) Bring residue to volume (100 ml CCl_4). This becomes the SIMULATED STANDARD SOLUTION (Ar) for the oil with unknown identity. Run IR as with SAMPLE EXTRACT.
- (13) $\text{DISPERSED OIL IN WATER (mg/l)} = \text{Cr} \times \text{As}/\text{Ar}$.
- (14) Jet-air evaporate off the CCl_4 to dryness and bring residue up one or two ml (depending upon concentrations) with hexanes and run gas chromatographic analysis.
- (15) Bring to 50 ml volume in hexane and run UV-fluorescence analysis.

SURFACE WATERS OF JAMAICA BAY

With small quantities of total extractable hydrocarbons (organics) in sea water, slight modifications in the procedure were required. For example, 10 cm (path length) IR cells were utilized so as to obtain a sensitivity of 10X over the 1 cm cells. Twenty milliliters of CCl_4 were added to each sample bottle prior to collection, and then each sample was extracted twice with 25 ml of CCl_4 to ensure adequate extraction.

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The samples were shaken vigorously for one minute in separatory funnels. After phase separation, the bottom layer was drained through sodium sulfate

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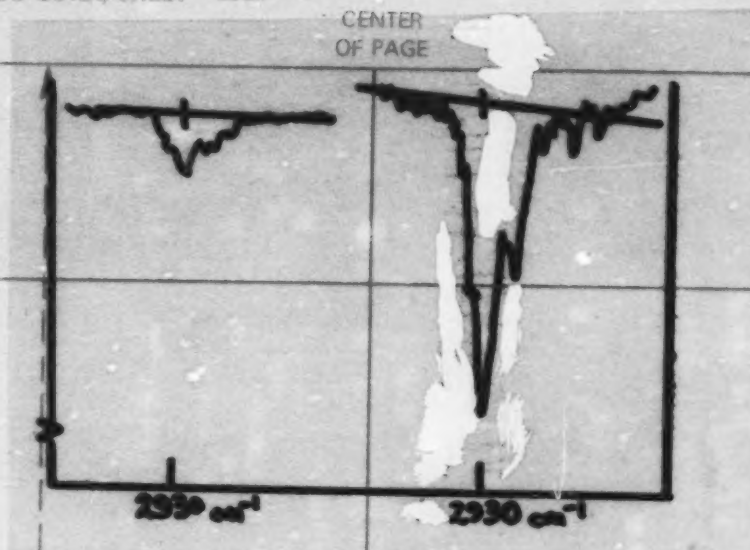


Figure 5. Oil absorbance IR band.

and collected in a tared 50 ml beaker. The extract solution became the **SAMPLE EXTRACT (As)**. Samples were scanned in the 3200 cm^{-1} to 2600 cm^{-1} region with an IR-Spectrophotometer using CCl_4 in the reference beam. Absorbance was again measured at 2930 cm^{-1} and the solution returned to the 50 ml beaker. The solvent was jet-air evaporated down to dryness and the residue's weight recorded.⁷⁸ This residue was brought to volume and became the **SIMULATED STANDARD SOLUTION (Ar)**. The solution was scanned in the range 3200 cm^{-1} to 2600 cm^{-1} for percent absorbance. Each surface water sample extracted was then analyzed by UV-Fluorescence spectroscopic techniques in a volume of 50 ml hexanes. The hexanes solvent was evaporated off and each sample was concentrated to 50 μl for gas chromatographic analysis.

MARINE ORGANISM (*Mya arenaria* L.)

Hydrocarbons are not unique to petroleum products, since marine organisms do synthesize specific hydrocarbons⁴⁸⁻⁵¹. The presence of waste petroleum hydrocarbons may be masked to some extent by the presence of naturally occurring hydrocarbons native to the organism itself. Such alteration processes as dissolution, biochemical oxidation and differentiation of hydrocarbon incorporation may also cause some difficulty in differentiation⁵². Therefore, with an analytical scheme involving a marine organism the specific identification parameters established, should be directed at detecting the presence of those classes of hydrocarbons unique to petroleum that are relatively unaffected by weathering and, which do not occur naturally in the organism.

Figure 6 is the procedure utilized for the extraction of waste petroleum in a marine organism. It was felt that by separation of the biological extracts into the fractions indicated, the specific hydrocarbons attributable only to oil pollution could be exhibited.

The clam tissue was homogenized with 50 ml of n-hexane (99 Mole % Pure; Fisher Scientific Co.) in a "Virtis 45" oilless blender (VIRTIS Co., Gardiner, N.Y.) at medium speed for three minutes. The solvent is jet-air evaporated

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15 shucked clams, *M. arenaria* L,
without internal fluids, size range
1-4 cm, frozen until analysis

VIRTIS BLENDER
homogenate tissue + 50 ml n-hexane

evaporate off solvent, add 3 x wet
tissue weight of Na_2SO_4 anhydrous
powder, mix and freeze for 24 hours

soxhlet extraction
for 6 hours in hexane

100 ml of extract - jet-air evapo-
rate solvent off - record weight
of residue in mg/100 ml

bring residue to 100 ml volume
hexanes - UV-fluorescence analysis

column chromatography

n-hexane
fraction
-saturates
-cyclic & non-cyclic
paraffins

benzene
fraction
cyclic paraffins
branched chain cpds
light aromatics

methanol
fraction
aromatics
PNA's, heterocompds
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Figure 6. Extraction of hydrocarbons from an estuarine benthic organism.

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off, and three times the weight of tissue homogenate of Na_2SO_4 (anhydrous powder; Fisher Scientific Co.) is added. The mix is stirred with a spatula until the tissue is evenly distributed in the sodium sulfate. This entire blend is placed in a freezer for 24 hours. Upon removal from the freezer, the mix is added to a Soxhlet extraction thimble. The thimble (Whatman single thickness, cellulose thimbles) is pre-extracted in a Soxhlet with n-hexane for four hours to remove any contaminants. The original solvent is discarded and the thimble is extracted in fresh n-hexane for an additional two hours. A fluorescence check is conducted on this solvent by setting the sample sensitivity on the MPF-3 UV-fluorescence spectrometer at 30, exciting the sample at 290 mμ while scanning the emissions from 240 to 540 mμ. Emission intensity should not exceed 3% after this clean-up procedure.

Thimbles are then packed to within one-half inch of the top of the homogenate mix, and Soxhlet extracted in 150 ml of hexanes for a period of six hours. After this extraction period, 100 ml portions of the total solvent extract are removed and placed in 100 ml tared beakers. The solvent is stripped off and the residue weight recorded. This residue is brought to 100 ml volume with hexanes and UV-fluorescence analysis conducted.

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Total extracts obtained from organisms are composed of lipids and naturally occurring hydrocarbons coextracted along with any petroleum derived hydrocarbons that may be present. To better isolate the petroleum hydrocarbons, a column chromatographic technique was implemented to separate the original extract into basic saturate groups (normal, cyclic and branched paraffinic compounds) as well as an aromatic group (polynuclear, polycyclic aromatics and heterocompounds). This column chromatography technique utilized solvents to differentially elute desired fractions from hydrocarbon mixtures.

After the column has been prepared, it is prewet with 50 ml of hexanes. This entire volume is allowed to pass through the column (so as to calibrate a flow rate of approximately 2 ml/min with dry air pressure) until only a solvent meniscus remains at the top. A 2 ml volume of sample extract is added to the top of the meniscus and allowed to be absorbed. Fifty milliliters of n-hexane is immediately added to the column as the first eluate and 45 ml are collected in a tared 50 ml beaker. This is the HEXANE PORTION. Dry air is delivered to the top of the column so as to maintain a flow rate of approximately 2 ml/min. Once the entire hexane portion is absorbed, 50 ml of benzene is added and 45 ml are collected in a 50 ml beaker resulting in the BENZENE PORTION. Finally, 50 ml of methanol is added so as to elute the aromatic and heterocompounds, and is labeled the METHANOL PORTION. These solvent fractions are evaporated to dryness and weights of residues recorded. A flow-chart for the subsequent analyses of these fractions is shown in Figure 7.

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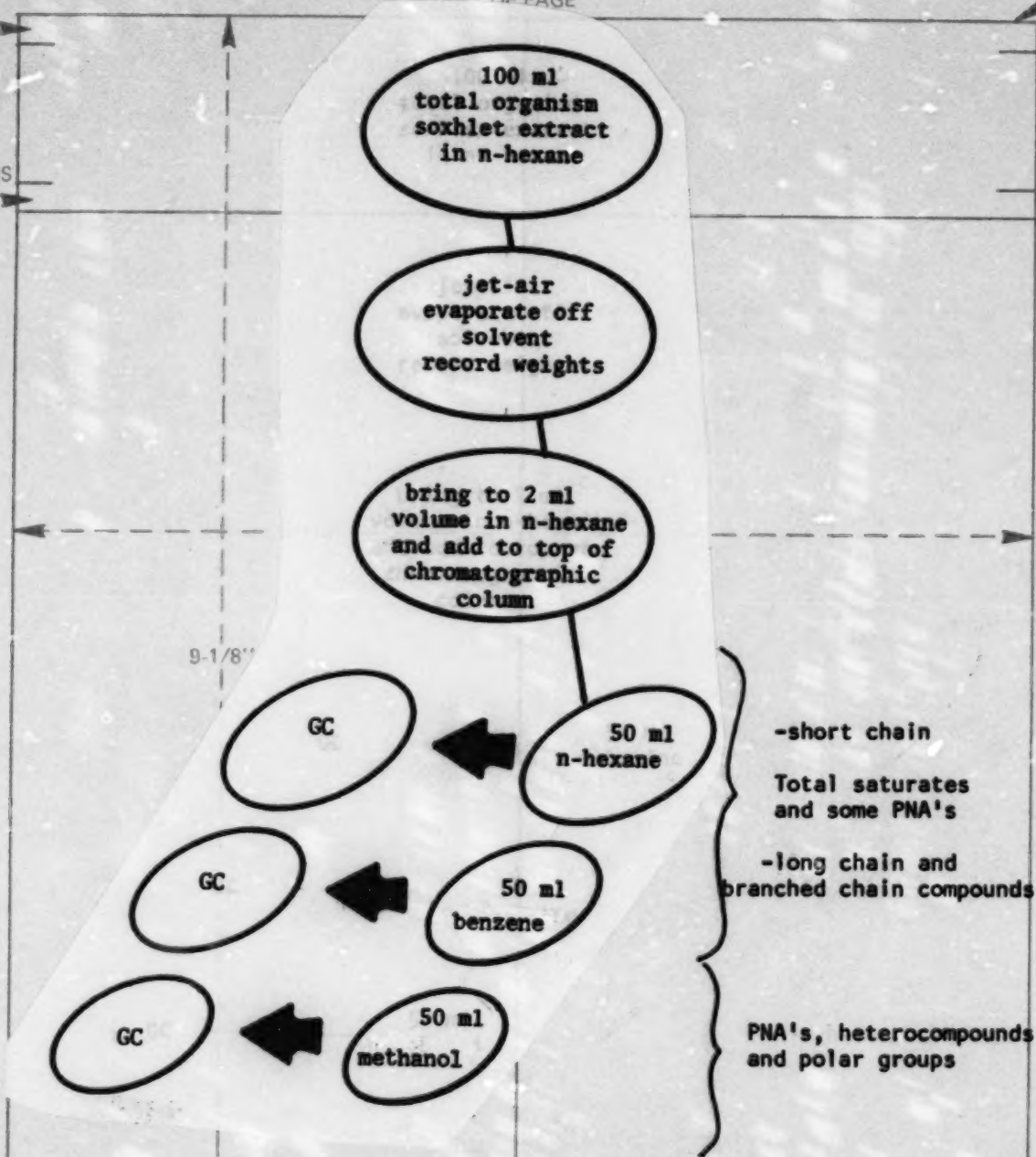
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Figure 7. Extraction and analysis of organism sub fractions: a flow diagram.

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SECTION 8

ANALYSIS OF SAMPLE EXTRACTS

GAS CHROMATOGRAPHY

Analytical Approach

Two qualitative approaches to the analysis of chromatograms generated by sample extracts were utilized in this study. The first sought to qualitatively match the chromatograms generated by environmental samples to those chromatograms obtained from a group of "on-hand" reference petroleum products including a waste crankcase oil. Specific chromatographic "profiles" of these reference standards were looked for in the environmental sample.

Figure 8 exhibits these petroleum entities and shows their unique chromatographic profiles. For example, chromatograms of the WCCO all exhibited a large unresolved envelope above the baseline. This envelope portion has been established⁵³ as being caused by the presence of a complex mixture of polynuclear aromatic hydrocarbon structures (PNA's). Gas chromatographic analyses of WCCO have indicated⁵⁴ the presence of a variety of 4- and 5-ring PNA compounds.

Also characteristic of the chromatograms generated by the WCCO standard is a "light-end" region containing those petroleum hydrocarbons with carbon numbers under C₁₂. These are accumulated in the crankcase after thermal breakdown of original polymeric additives and basic lubricating oil hydrocarbon constituents.

There is also the possibility of contamination from lower boiling range gasoline. Peaks atop the envelope portion of the chromatograms are attributable to mixtures of paraffinic, olefinic heterocompounds over a wide range of boiling points. Chromatograms of refined lubricating oils (Figure 8 B-E) do not exhibit the "light-end" or low molecular weight portion present in the WCCO chromatogram. These processed petroleum products usually do not contain many low boiling point n-alkanes because of dewaxing processes⁵⁵. However, many homologous isomers (branched alkanes) are present in petroleum products⁵⁶.

Mono- and polyalkylated benzenes and mixtures of polynuclear aromatics are not found normally in the environment, and because of their relative stability pose potential environmental threats. The gas chromatographic profiles generated by the constituents of refined petroleum products exhibit markedly different characteristics when compared to profiles of crude or fuel oils (see Appendix B for gas chromatograms of crude oils). The extensive unresolved envelope portion (UEP) can be attributable to the com-

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Figure 8. Chromatographic profiles of reference standards.

- A. Waste crankcase oil
- B. 10W/30 oil
- C. Transmission fluid

- D. Crude oil
- E. No. 2 fuel oil
- F. C₆-C₃₆ "SPIKE"

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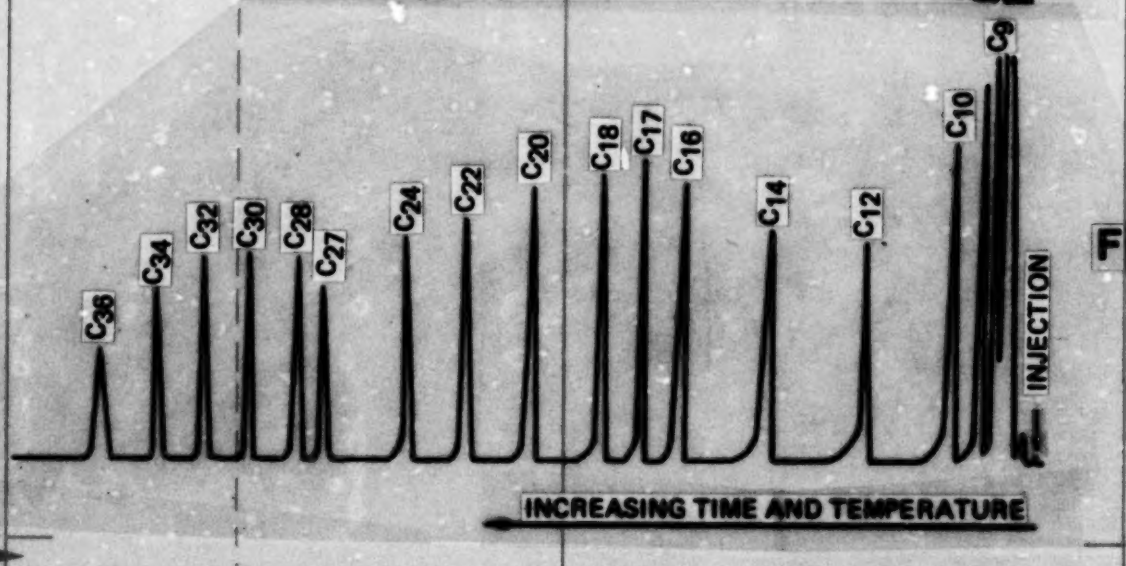
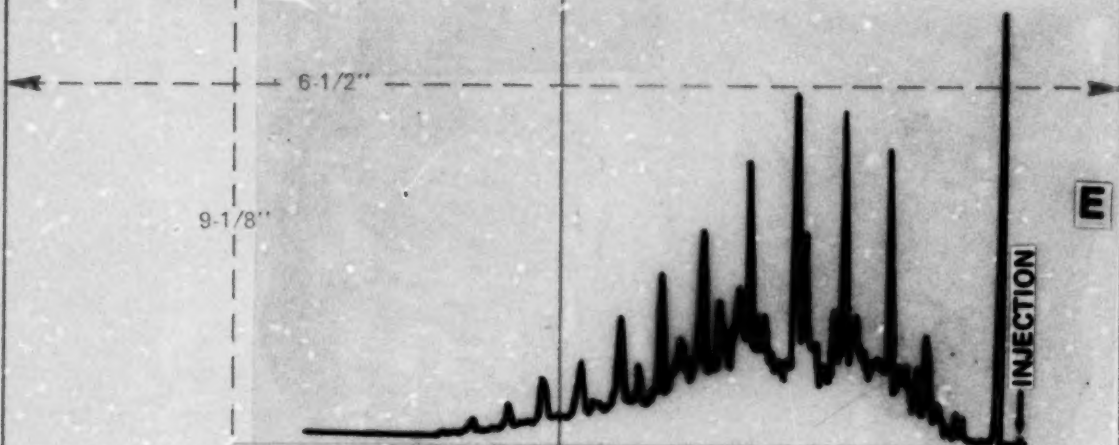
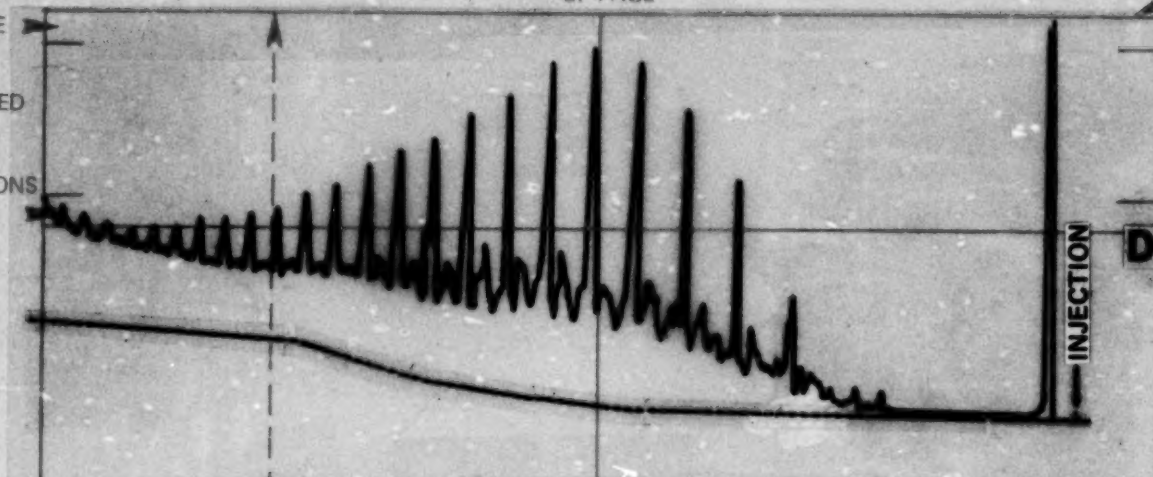
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plex, high boiling additives and natural constituents of these processed petroleum products. The high temperatures refined petroleum products are being subjected to in today's automobiles cause the breakdown of their substituent hydrocarbons. These high temperatures are similar to catalytic breakdown or "cracking" (the breaking down of large hydrocarbon molecules into smaller molecules by heat) and other refining processes (such as isomerization where there is an alteration of the arrangement of atoms in a molecule) to which the original crude oil may have been subjected. This is exhibited in chromatograms of fresh (non-weathered) WCCO by the presence of a "light-end" portion which is absent from chromatograms generated by the unused motor oils.

The rigors of environmental weathering will cause alterations to the WCCO profile. Volatile "light-ends" will be the first to be lost to evaporation. Bacterial degradation will utilize n-paraffins most readily and then sequentially utilize other petroleum derived hydrocarbons at a slower pace⁵⁷. Therefore, what chromatographic profile will look like for the detection of oil in the environment, will depend on the extent of weathering of this oil. Reference standard samples of WCCO, 10W/30, 20W/50 and transmission fluid (200 ml of each/1 of filtered sea water) subjected to 32 days of environmental weathering resulted in chromatograms exhibited in Figure 9.

The environmental persistence of the aromatic portion is indicated by the presence of the resultant envelope. That these high molecular weight paraffins and aromatic compounds are stable is confirmed by reports of samples taken from the Torrey Canyon disaster where it was found⁵⁸ that petroleum derived compounds above C₂₀ were stable after exposure to the environment for a month. Recent investigations⁵⁹ into the aromatic fractions in surface tars, show them to be composed mainly of alkylated naphthalenes. These compounds have been shown to be toxic to some marine species and to cause shifts in the species composition of phytoplankton. The recent Argo Merchant spill should be studied for such phytoplankton species shifts.

The second chromatographic approach involved the use of retention time indices. On a chromatogram the distance from the point of injection on the time axis to the peak of an eluted component emerging from the column is called the "retention time" for that particular component. Retention data are dependent upon the proper functioning of the gas chromatographic equipment as well as the inherent dependence upon column temperature, carrier gas flow rate and the affinity between sample component and the stationary phase. There are techniques to reduce variability to some degree in generated chromatograms such as injecting a sample while noting the retention values as well as the relative peak heights. A second injection of the sample is then made maintaining the same operating conditions, however, this time a standard C₆-C₃₆ "spike" is added to the sample solution. The retention times are noted again and any increase in peak heights of those sample components noted on the previous chromatograms by the corresponding reference carbon compound, should indicate its presence in the sample. The use of retention data was also utilized to detect hydrocarbons present in the organism extract samples after these extracts were eluted through an absorption column and separated into specific hydrocarbon fractions. The chromatograms generated by this technique will be discussed in another section of this report.

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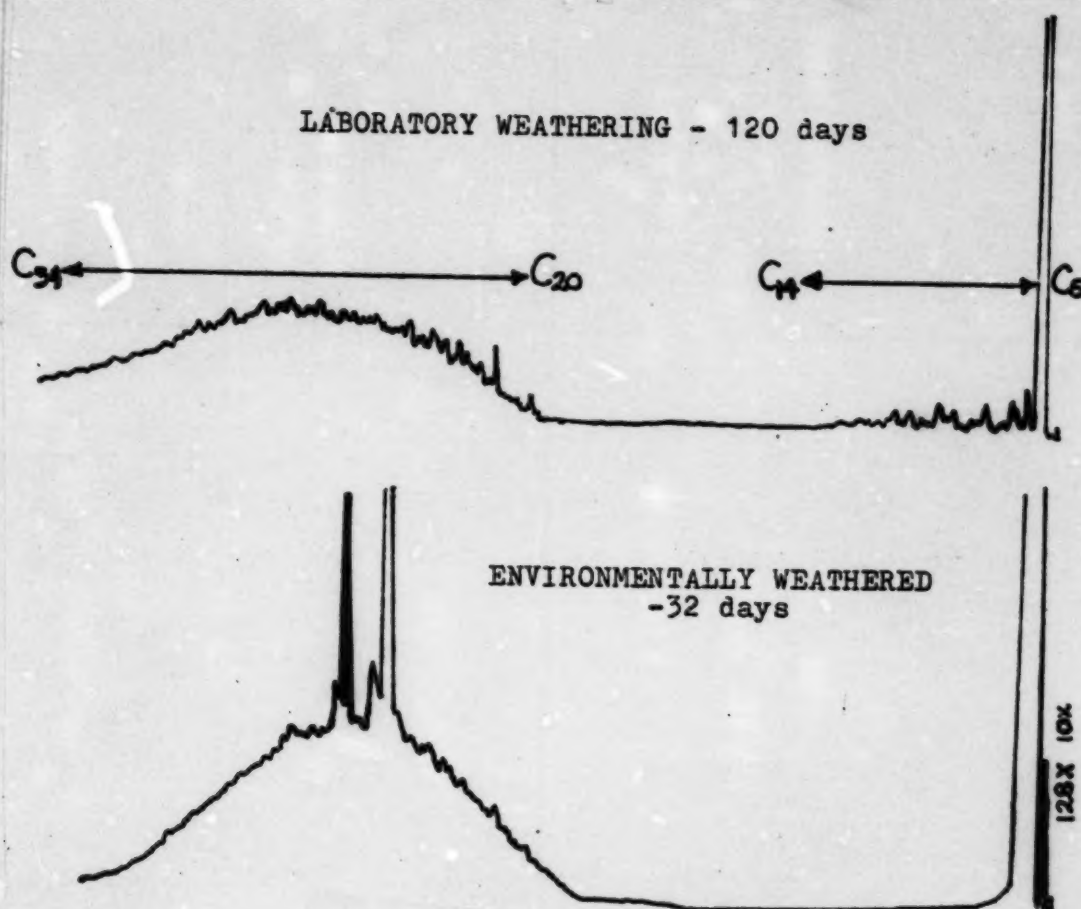


Figure 9. Gas chromatograms of weathered waste crankcase oil.

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UV-FLUORESCENCE SPECTROPHOTOMETRY

Analytical Approach

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All petroleum products will fluoresce when excited by ultraviolet light due to the presence of a mixture of hydrocarbon compounds with multi-ring configurations, such as fused-ring polynuclear aromatics⁶⁰. Whether or not an environmental sample was considered containing waste petroleum pollutants was determined by its profiles ability to "correlate" visually with profiles generated by reference sample oils under the same analytical conditions. Each reference sample oil (10 mg/100 ml n-hexane solutions 10W/30, 20W/50, transmission fluid and waste crankcase oil) was excited at 290 mu, while scanning the emission spectrum from 240 to 540 mu (Figure 10). Previous investigators⁶¹ had utilized 340 mu as the excitation wavelength for the characterization of petroleum entities, however it has been shown⁶² that Raman scattering, a peak generated by inherent characteristics of the solvent itself, at that frequency will obscure and otherwise alter the fluorescence profile to a degree that sample differentiation is made difficult. Excitation of the various petroleum products utilized in this project at 290 mu allowed for greater differentiation and for unique characterizations.

A synchronous excitation fluorescence spectroscopic technique was implemented for sample analysis⁶³. Each standard oil was excited at successive excitation wavelengths (at 20 mu intervals) from 240 mu to 440 mu while scanning for the maximum fluorescence emission at each of the respective excitation wavelengths. Each maxima peak can be utilized as a point to be plotted graphically generating a "fluorescence maxima profile" (FMP) for each sample (Figure 11). Once the FMP's for reference standard oils are obtained and the environmental sample FMP's generated, a qualitative correlation can be made. A correlation was determined visually by comparing the FMP plots of known oils to the maxima profile plots of the environmental samples (Figure 12). If these maxima profiles "fit" each other (Figure 13), then the presence of a waste petroleum product is established for the particular sample under investigation. This passive detection scheme depends upon the presence of fluorescent petroleum compounds, such as polynuclear aromatics and permits the differentiation between waste lubricating petroleum products and other petroleum entities. In addition, the ability to differentiate between a lubricating oil and a crude or fuel oil⁶⁴ as well as the ability to differentiate between different motor oils by UV-fluorescence spectroscopy have been documented⁶⁵ and supports the aforementioned criteria.

Once a WCCO enters the environment, it is immediately subjected to environmental weathering processes. Evaporation and bacterial degradative processes begin immediately. If this waste petroleum product remains in the environment long enough it will begin to lose some of its passive identification characteristics (i.e. "light-ends" are lost in gas chromatograms of weathered WCCO). Weathering has less of an overall effect on fluorescence analysis due to the environmental resistance of polynuclear aromatics (PNA) and aromatic portions of waste automotive lubricants. Since ppb levels of PNA's will be detected by fluorescence analyses, those sample profiles which exhibit similar emission characteristics as those profiles generated by standard oils, allow for their correlation.

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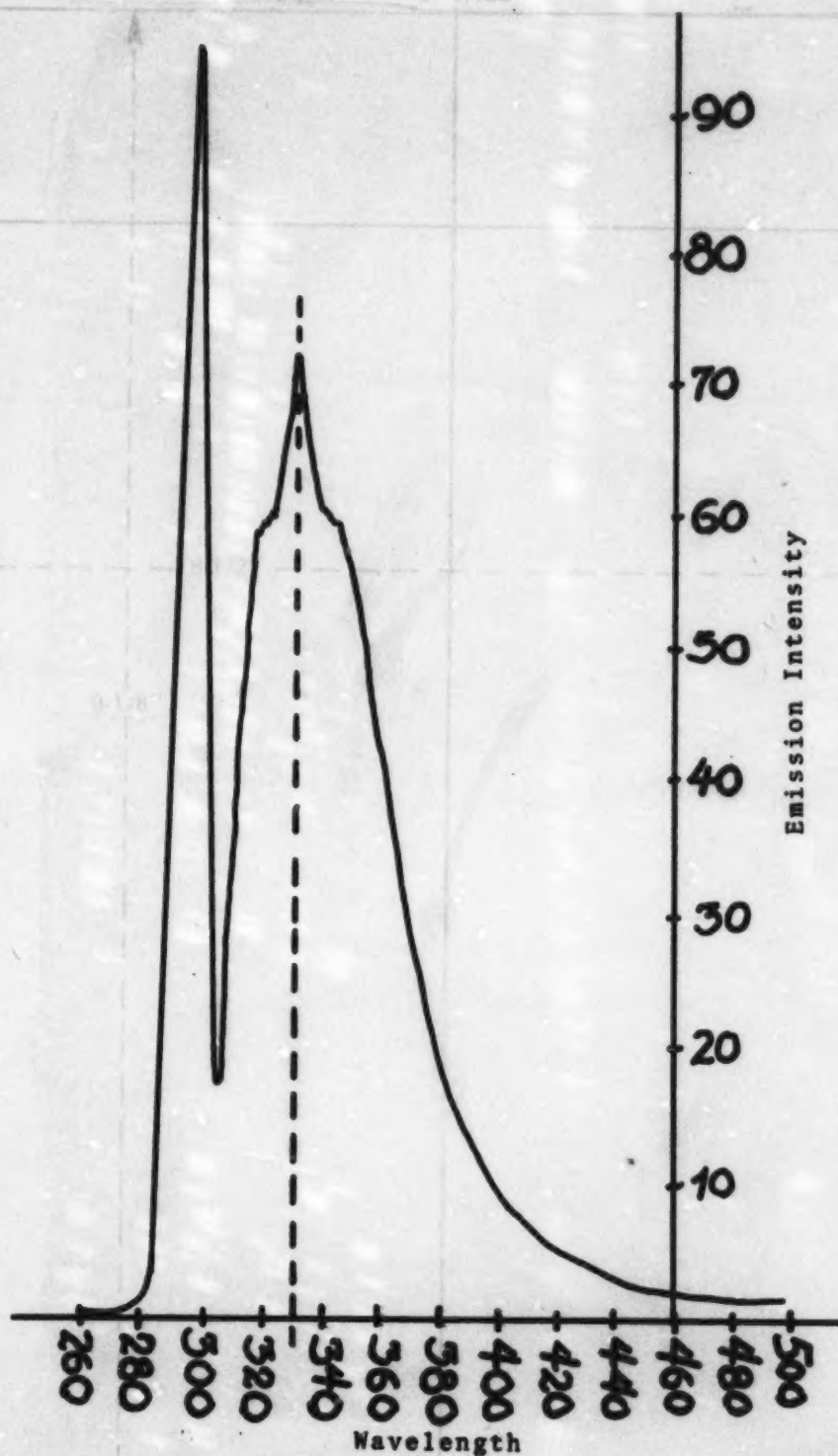


Figure 10. "Reference Standard" waste crankcase oil.

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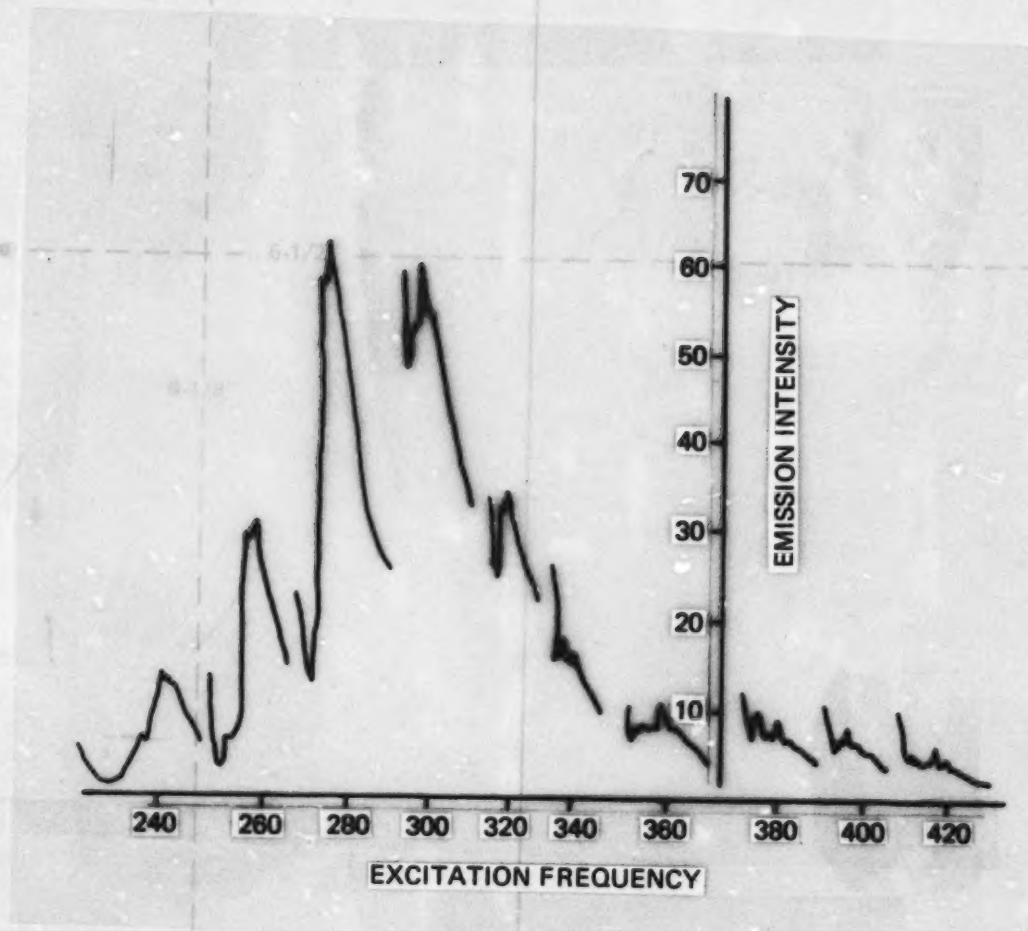


Figure 11. Fluorescence maxima profile (FMP) for WCCO.

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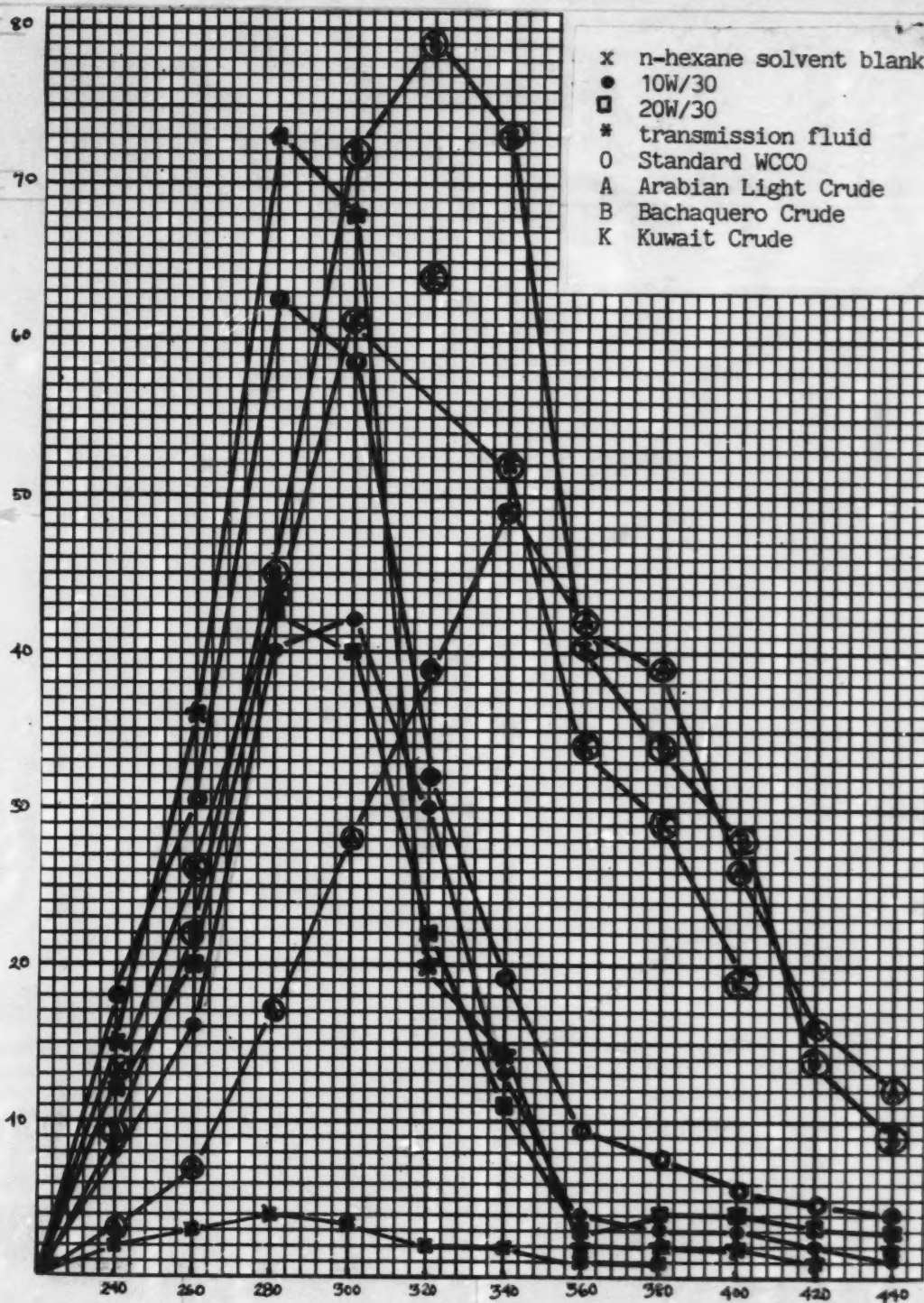


Figure 12. Refined petroleum product's FMP's.

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EMISSION INTENSITY

KEY

- = WCCO Standard
- = 28th. Ward
- △ = Jamaica
- x = Coney Island
- = Rockaway

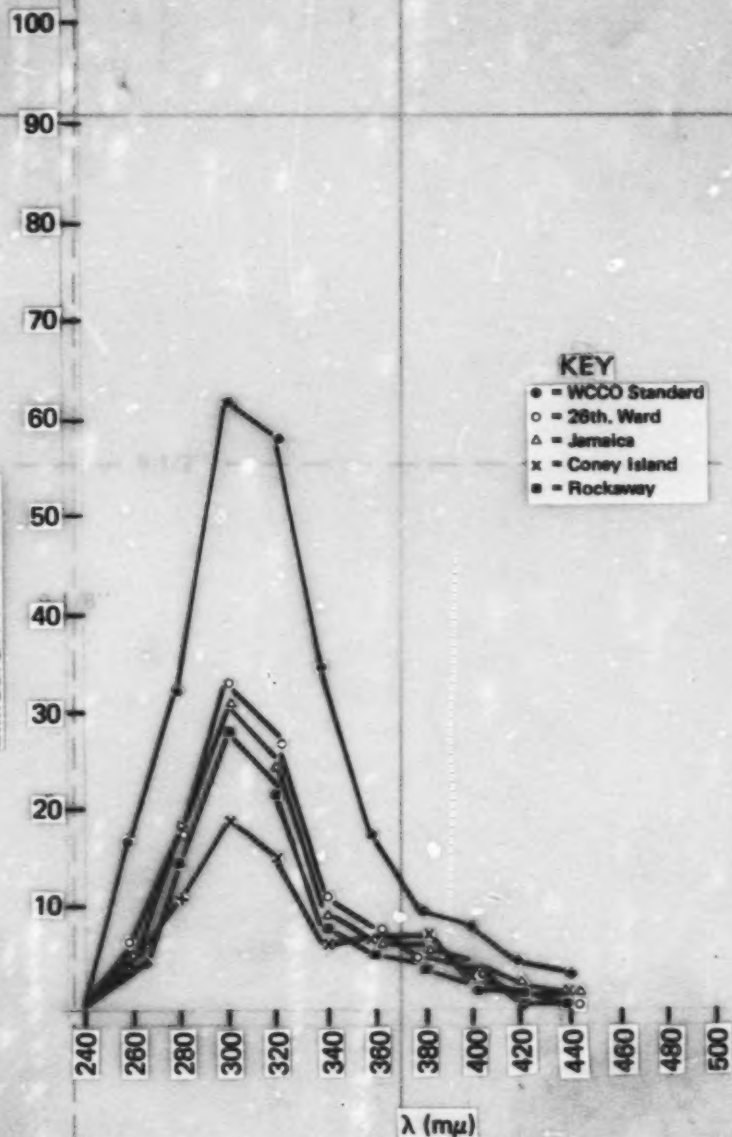


Figure 13. Fluorescence Maxima Profiles (FMP) for environmental sample extracts.

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In every case where a sample's profile met the qualitative criteria established by the reference samples, it was noted in a "correlates" column. When the profiles generated were inconsistent with the qualitative criteria for a correlation, it was noted in a "slight correlation" category. It should be emphasized that the correlation criteria are purely formulative in that direct source identification (whether gas station, marina, etc.) of particular petroleum waste products could not be established by this analysis technique. The fluorescence method was developed to identify suspect oils using known and reference oil samples. Further investigation into the effectiveness of these methods in the detection of unknown oils is needed. Correlation is based solely upon profiles generated and information gained through fluorescence analysis of reference samples. In some cases the environmental samples which exhibited fluorescence responses to that of the standard WCCO, also exhibited additional fluorescence responses similar to other oils. It was for this reason that a category entitled "slight correlation" was utilized instead of "no correlation", since there was the possibility of the presence of a mixture of petroleum entities within the sample extracts. The source of these oils could be from home heating fuels discarded as tank-bottom wastes, since No. 4 and No. 6 fuel oils are utilized as heating fuels for housing complexes in this area. Yet, fluorescence differentiation of these fuel oils and waste automotive lubricants can be clearly observed in 290 mμ excitation emission profiles (Figures 14 and 15).

Operating Procedures

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In the operation of the UV-fluorescence spectrophotometer, low fluorescence silica cells were utilized. All solvents were analyzed for contaminants by fluorescence at maximum sensitivities before use. Figure 16 is a schematic for the fluorescence analysis procedure as well as the instrument settings utilized.

GAS CHROMATOGRAPHY - MASS SPECTROSCOPY (GC-MS) AS A CONFIRMATION METHOD

The use of mass spectroscopy for the analysis of hydrocarbons derived from petroleum products has been well established⁶⁶⁻⁶⁸. Use of high resolution mass spectroscopic equipment has enabled investigators⁶⁹ to determine as many as 2900 components in a single petroleum fraction sample. For such extensive data acquisitions, the use of a computerized system has greatly increased speed of analysis and identification^{70,71}. Fractions obtained from column chromatography of marine organism extracts were evaporated to approximately 50 ul with 1-5 ul portions being injected into the system.

The following list outlines the GC-MS computerized system utilized.

Column dimensions

5 foot x 2 mm ID, glass, packed 3% OV-1 on Chromsorb W.

Program

Temperature programmed 100°C to 280°C at 6°C/min, run isothermally at 280°C for approximately 10 minutes.

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Carrier Gas

Helium; flow at 1.5 ml/min at column outlet.

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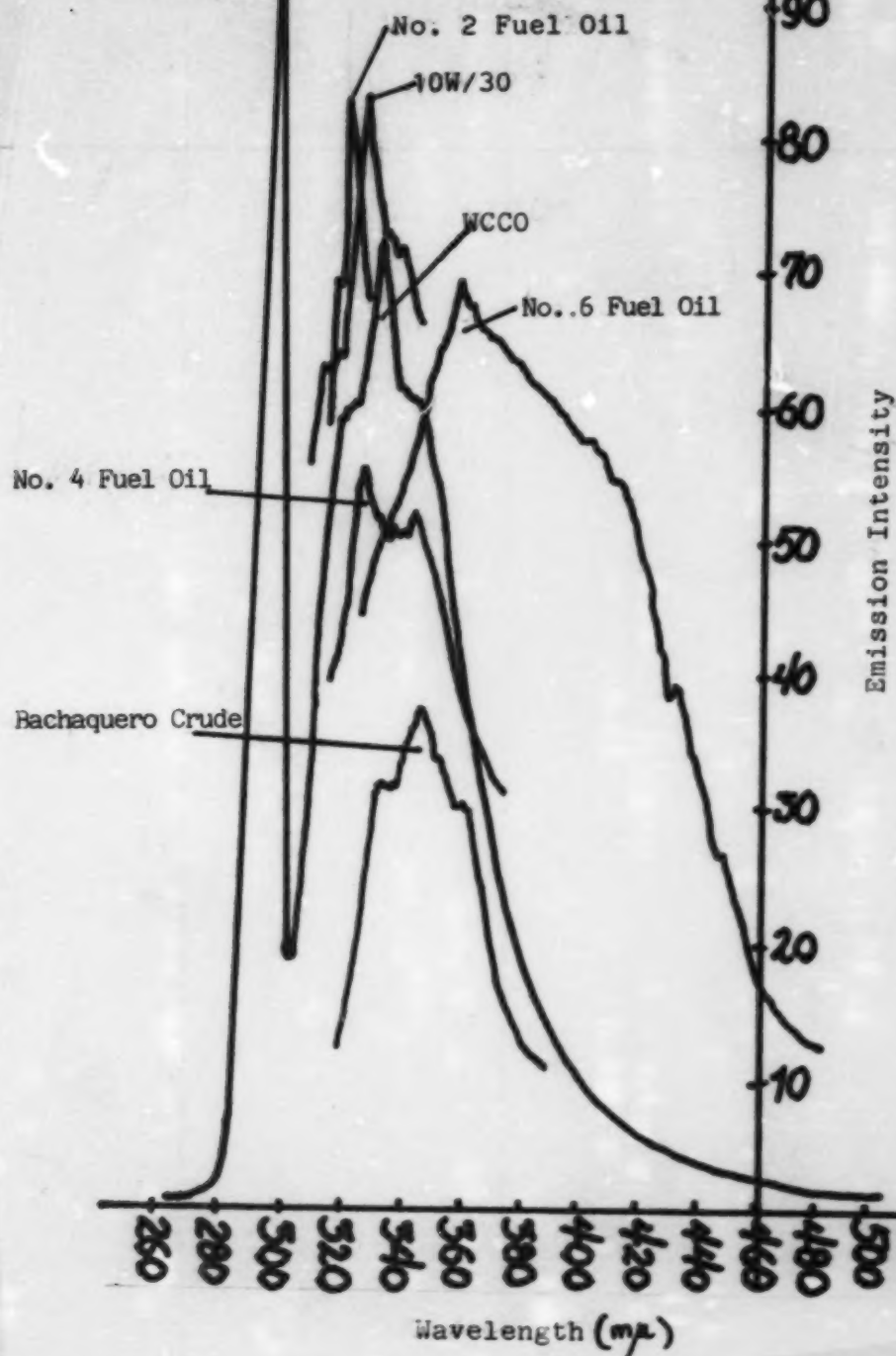
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Figure 14. "Reference Standard" samples.

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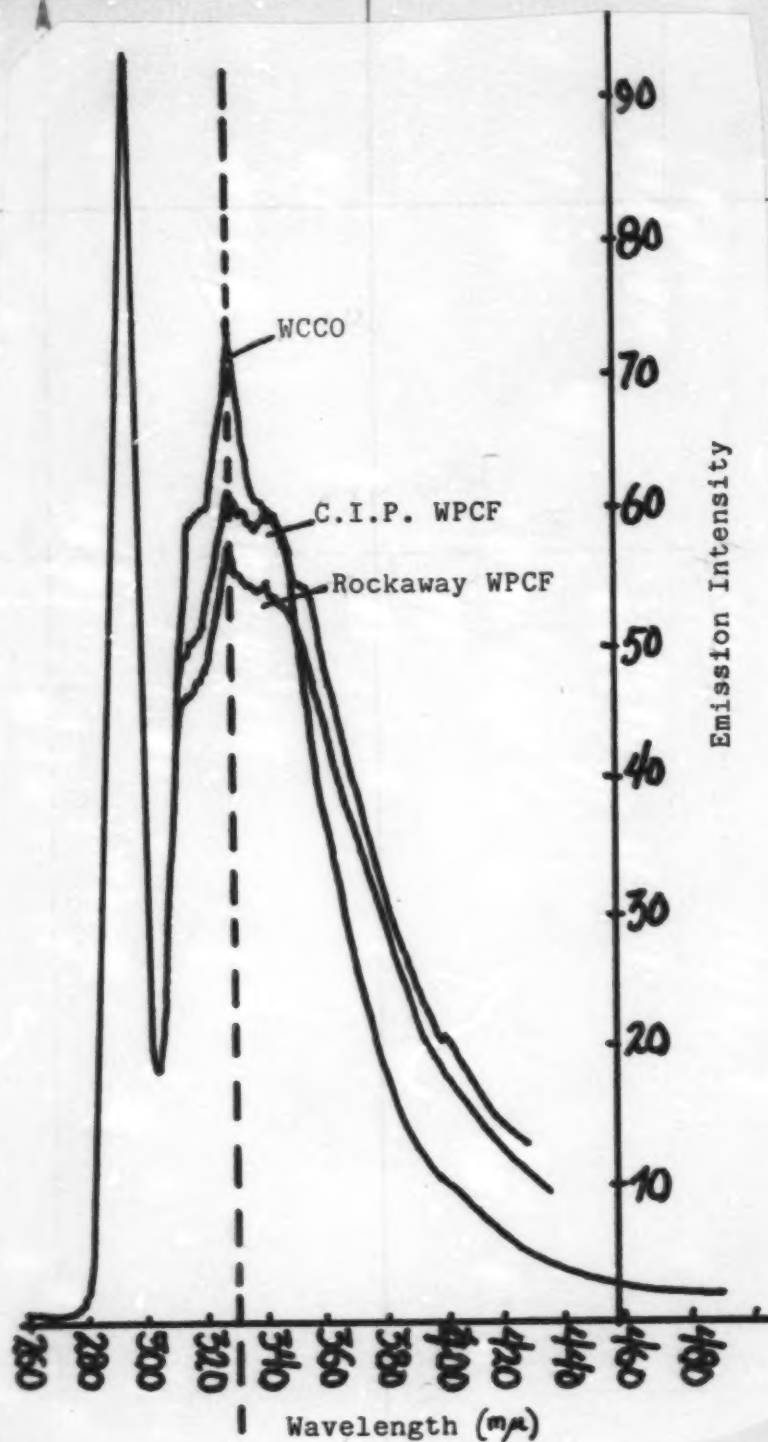
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Figure 15. Correlation with WCCO reference standard.

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Excitation at each wavelength between
240 and 440 mu; scan maximum emissions
at each excitation frequency
Excitation slit - 12
Emission slit - 10
Scan speed - 4
Sample sensitivity settings - 1.0 to 3.0

Excitation at 290 mu
Scan emissions from 240 to 540 mu
Scan speed - 3
Excitation slit - 12
Emission slit - 3
Sample sensitivity not to exceed 10

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Fluorescence Profiles



Figure 16. Fluorescence analysis procedures.

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Mass Spectrometer

Computerized Finnigan Gas Chromatograph Quadrupole Mass Spectrometer
Combination, Model 1015.

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It should be noted that the column in this particular GC-MS system did not have the resolving power of the SCOT OV-101 columns utilized under the regular chromatographic analysis of this project. For this reason, mass spectral data for identification was restrained to some degree, and only a few compound classes were tentatively identified. Subsequent studies in this area should integrate SCOT columns with GC-MS computerized networks similar to work done by Raymond and Gulochon⁷².

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SECTION 9

RESULTS

WASTEWATER EFFLUENTS

The collection of WPCF's final effluents emptying into Jamaica Bay, ran for a period commencing September 10, 1973 extending through November 5, 1973 with a total of thirty-nine samples being taken. Table 5 gives the quantitative results of the CCL_4 extraction and infrared analysis of these samples. Table 6 gives the hexane extractable materials (HEM) that the City of New York, Bureau of Water Resources had recorded since August 1972. As of May 1973 the City had utilized an infrared quantification method for analysis and records the results as "oils and grease" in its monthly records for each WPCF.

Four WPCF final effluent extracts were analyzed by gas chromatography. Table 5 indicates those samples chosen at random and analyzed by the two gas chromatographic techniques outlined in this project. Each sample chromatogram was observed for unique qualitative characteristics as well as for retention data of resolved peaks. A spiked sample (effluent sample plus $\text{C}_6 - \text{C}_{36}$ n-paraffin standards) was then injected, again noting retention times. In all cases (Figure 17) chromatograms indicated an unresolved envelope portion above 200°C . Spiked samples exhibited increases in peak heights for a major portion of the resolved peaks. Those peaks that occurred between standard peaks were labeled.

Normal paraffins are removed as a common practice of petroleum refineries since they give a waxy consistency which is undesirable in lube oil products. This dewaxing process usually removes a portion of the high molecular weight paraffins above C_{40} , as well. Some low molecular weight paraffins do however remain in the oil product to aid in the maintenance of proper viscosity. The presence of normal paraffins of the $\text{C}_6 - \text{C}_{36}$ standard solution were indicated by increased heights of extract components in generated chromatograms. Peaks on chromatograms which occurred between normal paraffin peaks are attributable to the presence of series of isomeric compounds and branched chain compounds.

Another criteria used to detect waste petroleum hydrocarbons in chromatographic profiles is to exhibit the partially resolved C_{17} -pristane, C_{18} -phytane hydrocarbon peak-pairs indicative of petroleum contamination. Insufficient data was recorded here. Some indication of these petroleum derived hydrocarbons were illustrated in some sewage effluent chromatograms (Figure 17 26th Ward gas chromatogram).

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Each of the WPCF effluent sample extracts were analyzed by UV-fluorescence spectroscopy and the results of correlation with profiles generated by reference oils under the same analytical parameters are shown in Table 7.

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TABLE 5. IR QUANTIFICATION OF TOTAL EXTRACTABLES (HYDROCARBONS) FROM WPCF TREATED EFFLUENTS*

Water pollution control facility	Date									
	9/10	9/15	9/17	9/24	9/29	10/1	10/8	10/15	10/22	10/29 11/5
Coney Island Plant	1.5	16.4	7.1	2.0	3.5	15.6	3.0	39.8	10.5	41.6 8.6
26th Ward Plant	29.7	20.0	34.9	28.9	22.9	12.3	19.2	19.1	9.3	-----
Jamaica Plant	----	10.7	12.0	7.2	5.3	4.7	9.6	4.6	9.4	14.2 18.8
Rockaway Plant	----	----	4.9	1.3	4.7	0.5	10.0	13.8	8.5	7.7 3.2

* all values in mg/l

☐ = GC analysis

TABLE 6. "OILS AND GREASE" - HEXANE EXTRACTABLES*

WPCF										
	8/72	9/72	10/72	11/72	12/72	1/73	2/73	5/73	6/73 7/73	8/73 9/73
Coney Island Plant	13.0	6.0	7.0	15.0	6.0	10.0	11.0	4.0	11.8 19.7	6.4 11.3
26th Ward Plant	21.0	12.0	7.0	24.0	37.0	30.0	19.0	30.0	180. 250.	410. 280.
Jamaica Plant	7.0	9.0	11.0	18.0	8.0	20.0	7.0	20.0	430. 280.	115. 180.
Rockaway Plant	11.0	9.0	7.0	11.0	4.0	9.0	11.0	80.0	170. 150.	95. 160.

* all values in mg/l; from Ward Island, Bureau of Water Resources, City of New York

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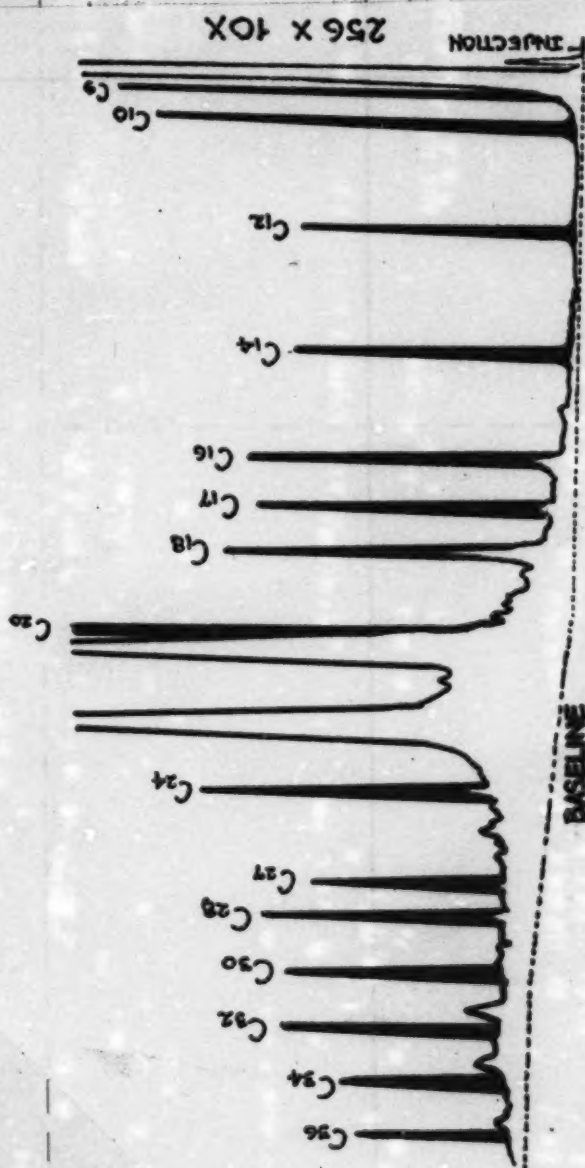
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* dark areas are C₆-C₃₆ spike above peak heights - 26th Ward STP

Figure 17. Gas chromatogram of sewage effluent extract*.

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TABLE 7. UV-FLUORESCENCE DATA FROM WATER POLLUTION CONTROL FACILITIES

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Date	Sample	Fluorescence Maxima Profile Fit		280 - 300 mu Maxima Region Fit		332 mu Peak Fit
		Correlate	Slight correl.	Correl.	Slight correl.	Slight Correl. correl.
1973						
9/7	26th	+		+		+
	CIP	+		+		+
	Jam	+		+		+
	Rock	+		+		+
9/10	26th	+		+		+
	CIP	+		+		+
9/15	26th		+	+		+
	CIP		+	+		+
	Jam	+		+		+
	Rock	No	Sample	Available	This	Date
9/17	26th		+	+		+
	CIP	+		+		+
	Jam	6-1 1/2"		+		+
	Rock	+		+		+
9/24	26th	+		+		+
	CIP	+		+		+
	Jam	+		+		+
	Rock	9-1 1/8"		+		+
9/29	26th	+		+		+
	CIP	+		+		+
	Jam	+		+		+
	Rock	+		+		+
10/ 1	26th		+	+		+
	CIP		+	+		+
	Jam	+		+		+
	Rock	+		+		+
10/ 8	26th		+	+		+
	CIP		+	+		+
	Jam	+		+		+
	Rock	+		+		+
10/15	26th	+		+		+
	CIP	+		+		+
	Jam	+		+		+
	Rock	+		+		+
10/22	26th	+		+		+
	CIP	+		+		+
	Jam	+		+		+
	Rock	+		+		+
10/29	26th	No	Sample	Available	This	Date
	CIP		+	+		+
	Jam	+		+		+
	Rock	+		+		+
11/ 5	26th	No	Sample	Available	This	Date
	CIP	+		+		+
	Jam	+		+		+
	Rock	+		+		+

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The sensitivity of fluorescence spectroscopy to polynuclear aromatics (PNA's) permits the unique characterization of different petroleum products in the environment. To see if the weathering phenomena would affect identification criteria for WCCO, fluorescence analysis was conducted on the various fresh automotive lubricating oils weathered in filtered sea water on the roof of the laboratory for a period of 32 days. Even after this weathering period, differentiation of lubricating oils from other petroleum products was accomplished by use of the fluorescence techniques outlined in this project. It has been demonstrated⁷³ that a variety of weathered oil products do not lose their specific identification characteristics under UV-fluorescence analysis. Profiles may in some instances exhibit a decrease in intensity due to concentration factors (Figures 18 and 19). Crude and fuel oils weathered for a period of 5 days open to air exhibited no change in identification characteristics in analyses performed at the Industrial Waste Treatment Laboratory, U.S. EPA, Edison, New Jersey. The lubricating oils weathered for this project did show a decrease in fluorescence intensities. When these samples were excited at 290 mμ, the resultant emission profiles were not altered. The graphic representations of the maxima profiles obtained from wastewater sample extracts are shown in Figure 20.

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Jamaica Bay Surface Waters

The quantity of CCL₄ total extractables from each of the surface water samples collected in the Jamaica Bay area were in the milligram per liter concentration range. Average background levels of petroleum hydrocarbons in oceanic waters utilizing a similar solvent extraction method⁷⁴ have been estimated at 2 ug/l concentration levels. Greater than average concentrations or what was considered as high concentrations of petroleum hydrocarbons were in the range of 10 to 20 ug/l. Table 8 shows the values obtained for the Jamaica Bay surface waters to be above normal background levels of hydrocarbon concentrations. It should be emphasized that non-petroleum derived organic compounds are extracted with carbon tetrachloride and are not all lost during the jet-air evaporation step. Therefore, some portions of the extracts may be attributable to either biologically generated hydrocarbons or to some other petroleum entity. Care was taken to prevent contamination from waste petroleum products generated by the research vessel, extraction procedures and in storage.

Gas chromatographic analyses were made on all samples obtained on the January 8, 1974 sampling run through Jamaica Bay. Attenuation and sample injection quantities were the same for each sample so that visual comparison could be made on the chromatograms generated. It was noted that samples collected in the interior portions of the Bay showed significant increases in the broadness of unresolved envelope as compared to ocean samples. The characterization of specific peaks above the unresolved portion also increased. Specific attention should be directed toward the sample analyzed from the NYJ03 site whose chromatogram exhibited these characteristics. This sample concentration is attributable to petroleum hydrocarbon contamination. The chromatogram produced by the NYN09A sample indicated the least contamination. By maintaining the same attenuation settings and operating conditions, the chromatograms accentuate a gradient response of contamination much of which the fluorescence analysis indicates is attributable to petroleum (Figure 21).

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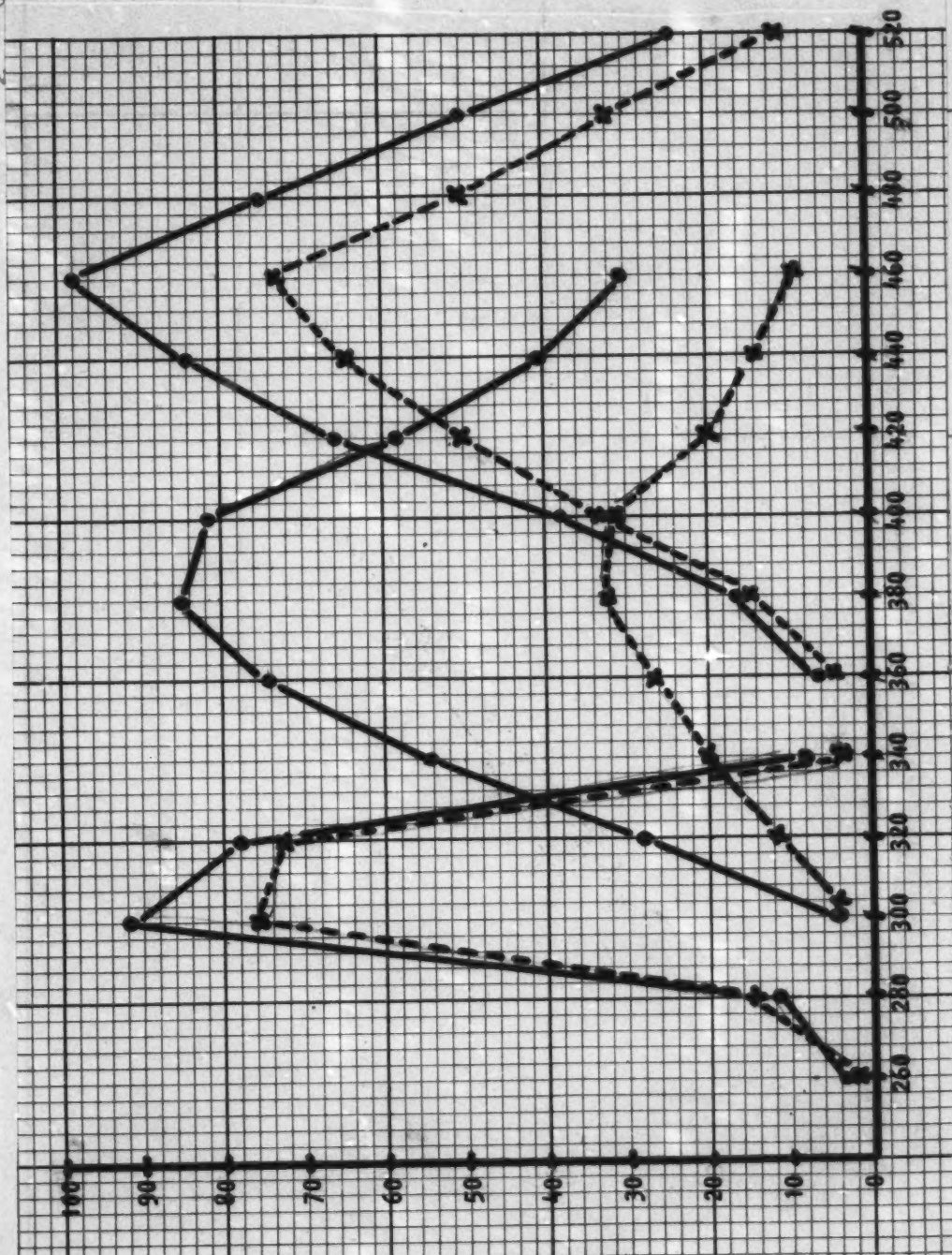
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• Non-weathered

X Weathered

Figure 18. Maxima profiles weathered and unweathered fuel oil simulated standards.

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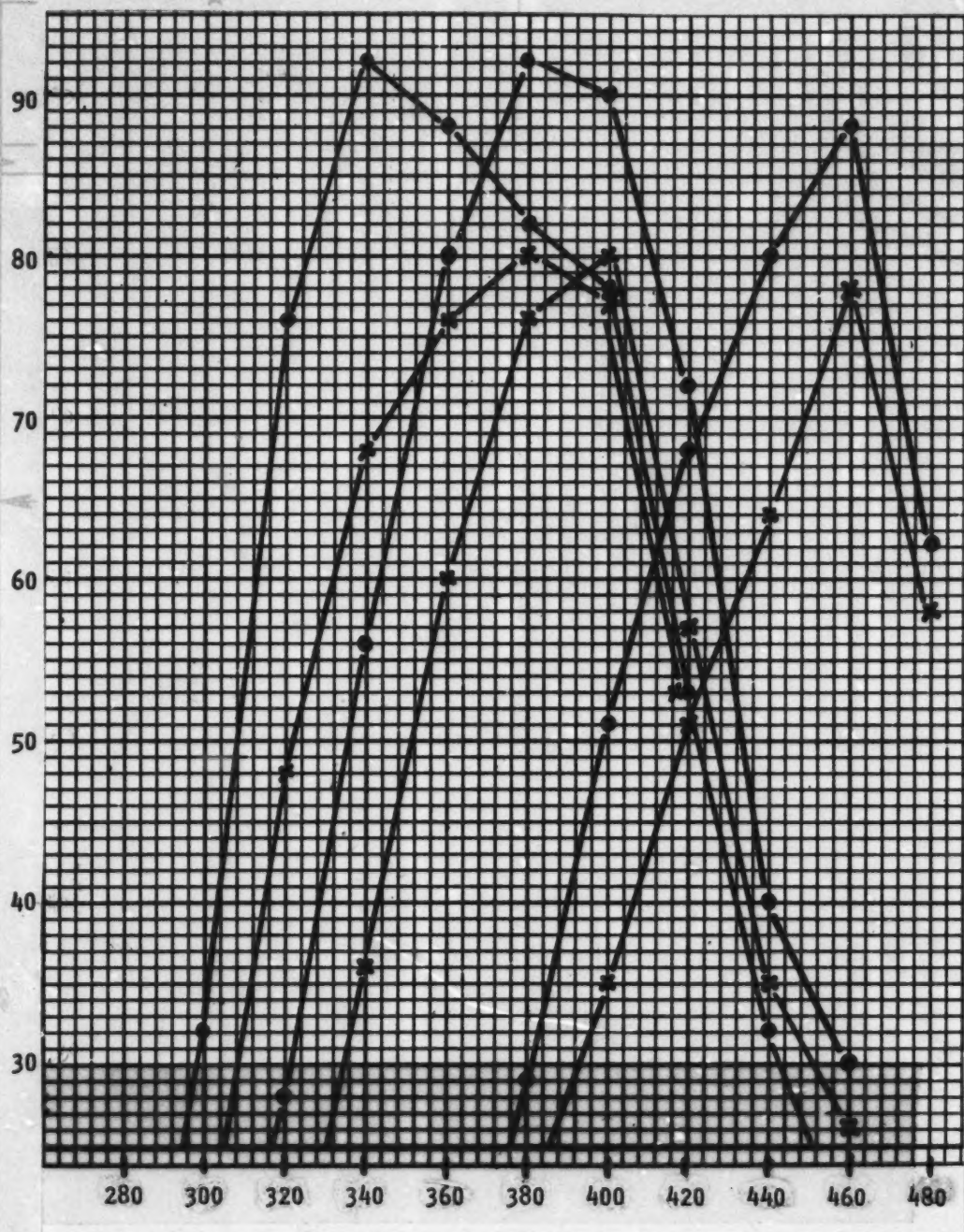
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X Weathered

• Non-weathered

Figure 19. Maxima profiles weathered and unweathered crude oils.

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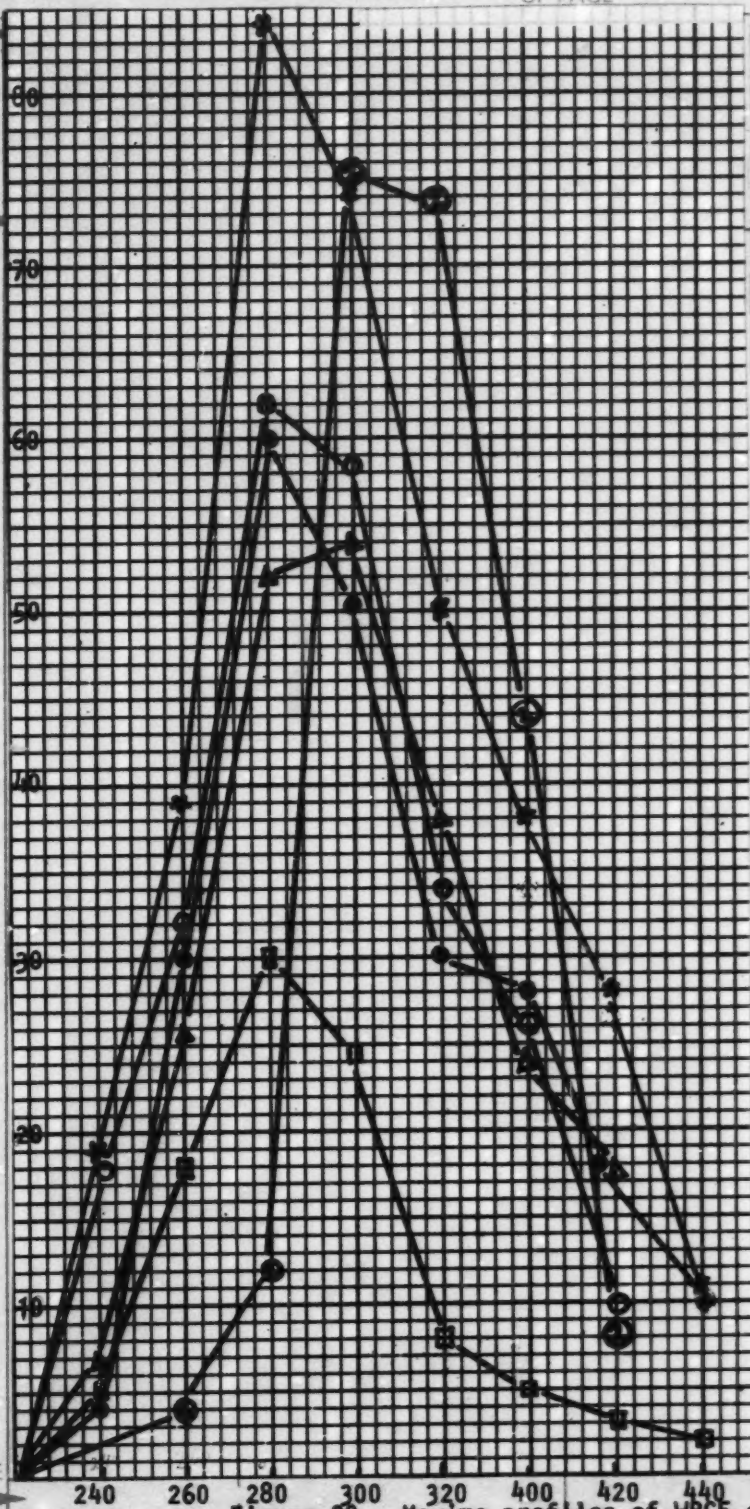
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- 2 #2 Fuel Oil
- 0 WCCO
- Jamaica STP (9/7/73)
- △ 26th Ward STP (9/10/73)
- * Rockaway STP (9/24/79)
- Coney Island STP (11/5/73)

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Figure 20. Maxima profiles of WPCF effluents.

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NYN09A

NYJ01

NYJ02

NYN16

NYJ03

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Figure 21. Surface water GS analysis.

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TABLE 8. JAMAICA BAY SURFACE WATER TOTAL CCL₄ EXTRACTABLES*

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Sample Site	November 7, 1973	January 8, 1974
NYN16	0.94	1.13
NYN09A	1.20	0.88
NYJ01	2.10	2.16
NYJ02	1.17	2.20
NYJ03	3.10	5.10
NYJ05	0.50	1.50
NYJ07	1.08	1.40

* all values in mg/l

Fluorescence analysis of surface waters reveal the presence of petroleum fractions in those samples from the Bay proper. Again, depending upon the degree of weathering to which the oil had been subjected the intensity of the fluorescence response varied. In no instance did any profile correlate with other types of petroleum entities such as the fuel or crude oils. In all cases when surface sample extracts were excited at 290 mμ, the generated emission profiles peaked at 332 mμ (Figure 22). Figure 23 exhibits the plotted fluorescence maxima profiles generated by the surface water extracts of Jamaica Bay for the two sampling runs (see Table 9.).

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TABLE 9. FLUORESCENCE CORRELATION DATA FOR SURFACE WATER SAMPLES

Date	Source	Fluorescence Maxima Profile Fit	Maxima Region Fit	332 mμ Peak Fit
		Correlate	Slight corr. Corr.	Slight corr. Corr.
11/7/73	NYN16		+	+
	NYN09A		+	+
	NYJ01		+	+
	NYJ02		+	+
	NYJ03	+	+	+
	NYJ05	+	+	+
	NYJ07		+	+
1/8/74	NYN16		+	+
	NYN09A		+	+
	NYJ01		+	+
	NYJ02	+	+	+
	NYJ03	+	+	+
	NYJ05	+	+	+
	NYJ07	+	+	+

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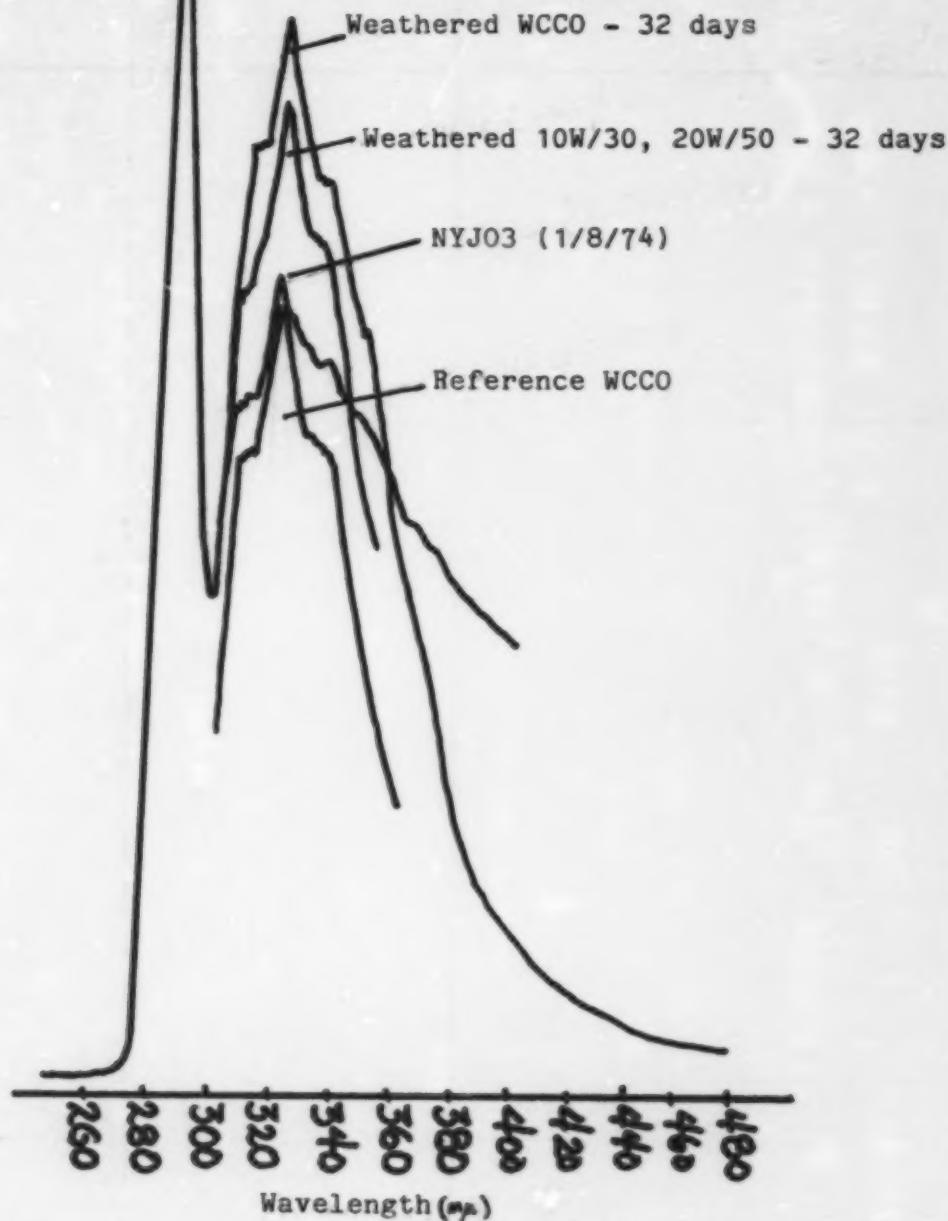


Figure 22. Correlation of emission spectra of surface water sample and weathered reference standards.

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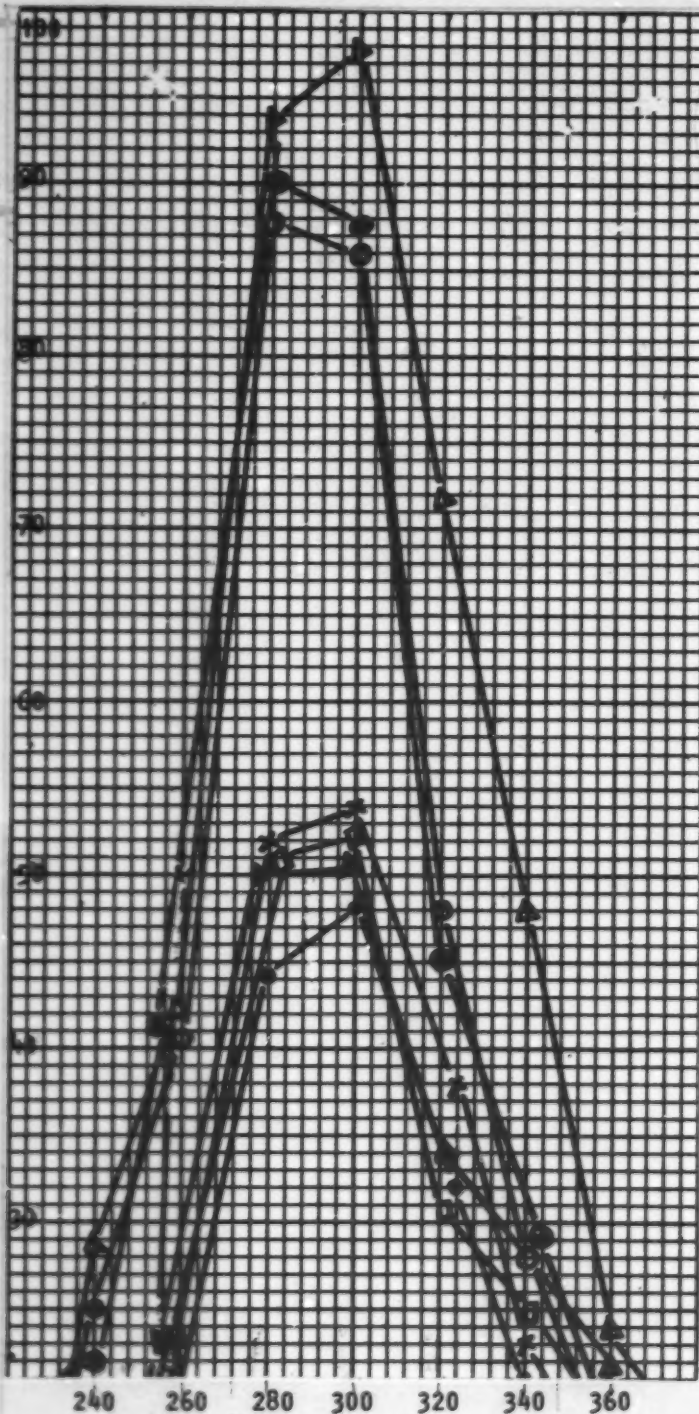
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- NYN09A
- X NYN16
- NYJ01
- NYJ02
- △ NYJ03
- ▲ NYJ05
- NYJ07

Note: See graphs - 1/8/74

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Figure 23. Maxima profiles for Jamaica Bay surface waters.

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Marine Benthic Organism (Mya arenaria)

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Table 10 shows column chromatographic results obtained for the Mya II extract (High Pollution Potential Sample). Column chromatography resulted in approximately 48% recovery of substituents for the Mya II sample. The test was duplicated with the Mya II (Table 11) extract (Low Pollution Potential Sample) at a slower flow rate (1 ml/min) for the eluted solvents. The results obtained using the slower flow rate exhibited approximately 80% recovery of hydrocarbon constituents from this total organism extract. The difference in recovery percentages indicate that a portion of the samples' hydrocarbons remained on the column. It was felt however, that because of the high pollution potential of the Mya II extract even with the relatively low recovery percentages, the eluted portions would lend themselves to the qualitative detection of petroleum hydrocarbons. Though recovery of the aromatics was not complete, gas chromatographic profiles exhibited a number of peaks for the aromatic portions. Subsequent quantitative studies should seek to recover as great a percentage of hydrocarbons as is obtainable.

It has been demonstrated⁷⁵ that hydrocarbons isolated from shellfish sampled in an area presumably free of petroleum contamination have all exhibited very simple compositions. Organisms have very specific biosynthetic pathways which favor the production of hydrocarbons with very specific carbon ranges. For example, some species of copepods exclusively contained hydrocarbons with 19 carbon atoms in a branched chain⁷⁶. Petroleum products, on the other hand, consist of a wide boiling range mixture of evenly distributed hydrocarbon constituents. Gas chromatograms exhibiting extensive unresolved portions are indicative of a samples content of these mixtures of branched, cyclic and aromatic compounds. Normal paraffins are the most abundant biological alkanes⁷⁷. Of the major types of hydrocarbons in organisms, olefins (alkenes) are the most abundant and aromatics generally the least abundant⁷⁸. Along with the mixture of simple normal and iso-alkanes, one or a few hydrocarbons exceed all others by several orders of magnitude in an organism's hydrocarbon pool⁷⁹. The presence of complex mixtures of polycyclic aromatic hydrocarbons in soils and sediments has been established⁸⁰. That they are not produced biologically but rather as the result of anthropogenic combustion process has also recently been expressed⁸¹.

Distribution of n-alkanes in biological tissue exhibit a preference of odd-numbered n-paraffins over even-number n-paraffins^{82, 83}. Indications of petroleum pollution arise when the odd:even ration approaches 1.0 as is the case of Mya II (1.02). The Mya III extract did suggest contamination by petroleum hydrocarbons, but to a lesser degree.

Thus, the appearance in gas chromatographic profiles of a complex, unresolved hydrocarbon envelope covering a wide boiling range, exceeded by numerous peaks indicative of homologous alkanes and their isomers, will suggest a mixed derivation of the hydrocarbons from petroleum pollution and biochemical sources.

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The chromatograms on the following pages indicated the presence of petroleum derived hydrocarbons in the body tissue of Mya arenaria obtained within Jamaica Bay. The aromatic portions of Mya II (HPP) exhibit a wide range of aromatic compounds with boiling points above 250°C. Mass-spectral analysis

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TABLE 10. HIGH POLLUTION POTENTIAL EXTRACT (HPP)

1/18/74; 100 ml of Mya II Total Extract	
Column Chromatography Results:	
100 ml beaker	47.5336 g
residue	47.7626 g
	.2291 g = 229.1 mg
50 ml n-hexane @ 2 ml/min	28.4420
collect 45 ml in #1 beaker	28.4446
	.0860 g
	2.6 mg
50 ml benzene @ 2 ml/min	27.4513
collect 45 ml in #2 beaker	27.5373
	.0860 g
	86.0 mg
50 ml methanol @ 2 ml/min	27.4444
collect 45 ml in #3 beaker	27.4660
	.0216 g
	21.6 mg
Total recovery = 110.2 mg or 48.1% extract.	

TABLE 11. LOW POLLUTION POTENTIAL EXTRACT (LPP)

1/25/74; 100 ml of Mya III Total Extract	
Column Chromatography Results:	
100 ml beaker	47.5748 g
residue	47.5989 g
	.0241 g = 24.1 mg
50 ml n-hexane @ 1 ml/min	27.5240
collect 45 ml in #1 beaker	27.5265
	.0025 g
	2.5 mg
50 ml benzene @ 1 ml/min	28.8972
collect 45 ml in #2 beaker	26.9017
	.0045 g
	4.5 mg
50 ml methanol @ 1 ml/min	27.3710
collect 45 ml in #3 beaker	27.3830
	.0120 g
	12.0 mg
Total recovery = 19.0 mg or 79% extract.	

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of the aromatic portion from Mya II (HPP) indicates the presence of substituted alkyl benzenes. These types of aromatic hydrocarbons have been found only in extremely small amounts or not at all in marine organisms. They predominate in the aromatic portions of petroleum products^{84, 85} (Appendix C, Mass Spectral Data). The saturate portions of Mya II (HPP) extract exhibit the presence of isomeric compounds probably of a branched paraffinic nature (Figure 24, Mya II Benzene portion). The Mya III extracts (LPP) (Figure 25) portion, was considerably simpler than the Mya II aromatic portion, indicating possibly less exposure to petroleum hydrocarbons outside the Bay than in the Bay.

The results of the fluorescence analyses on Mya arenaria extracts are shown in Table 12. Those samples collected from the Bay proper produced excellent correlations with reference oils. The Mya III extract did not correlate successfully with the reference standards, yet there was some indication of the presence of a petroleum fraction when one observed its maxima profile (Figure 26). When the Mya III extract was excited at 290 mu not only did an emission peak occur at 332 mu, but a peak of greater intensity occurred at 370 mu. This peak could be indicative of contamination from other petroleum pollutants derived from oceanic waters. For example residual fuel oils peak at 350-400 mu⁸⁶.

TABLE 12. FLUORESCENCE DATA FOR Mya arenaria L. EXTRACTS

Date	Source	Fluorescence max profile	Max region fit	290 mu excitation
1973		Correlation	Slight corr.	Corr. Sl. corr.
10/23	Mya I ^a	+	+	+
12/ 3	Mya II ^b	+	+	+
12/ 3	Mya III	+	+	+

a Collected at Egg Harbor, Jamaica Bay

b Collected at Diamond Point, Jamaica Bay

c Collected off Rockaway Point, Atlantic Ocean

If no recent oceanic oil contamination has occurred in the vicinity of Jamaica Bay, this result raises some interesting questions as to the origin of these residues. If these derived residues are attributable to past pollution incidents, the persistence of these petroleum derived hydrocarbons in the environment or their ability to become incorporated in biological tissue has been demonstrated by these results. Further investigation is needed to see whether or not similar data could result from some non-petroleum derived materials in such samples. Further study of specific compound identification is needed as well as work on the particular species distribution and diversity pattern in this petroleum hydrocarbon burdened ecosystem.

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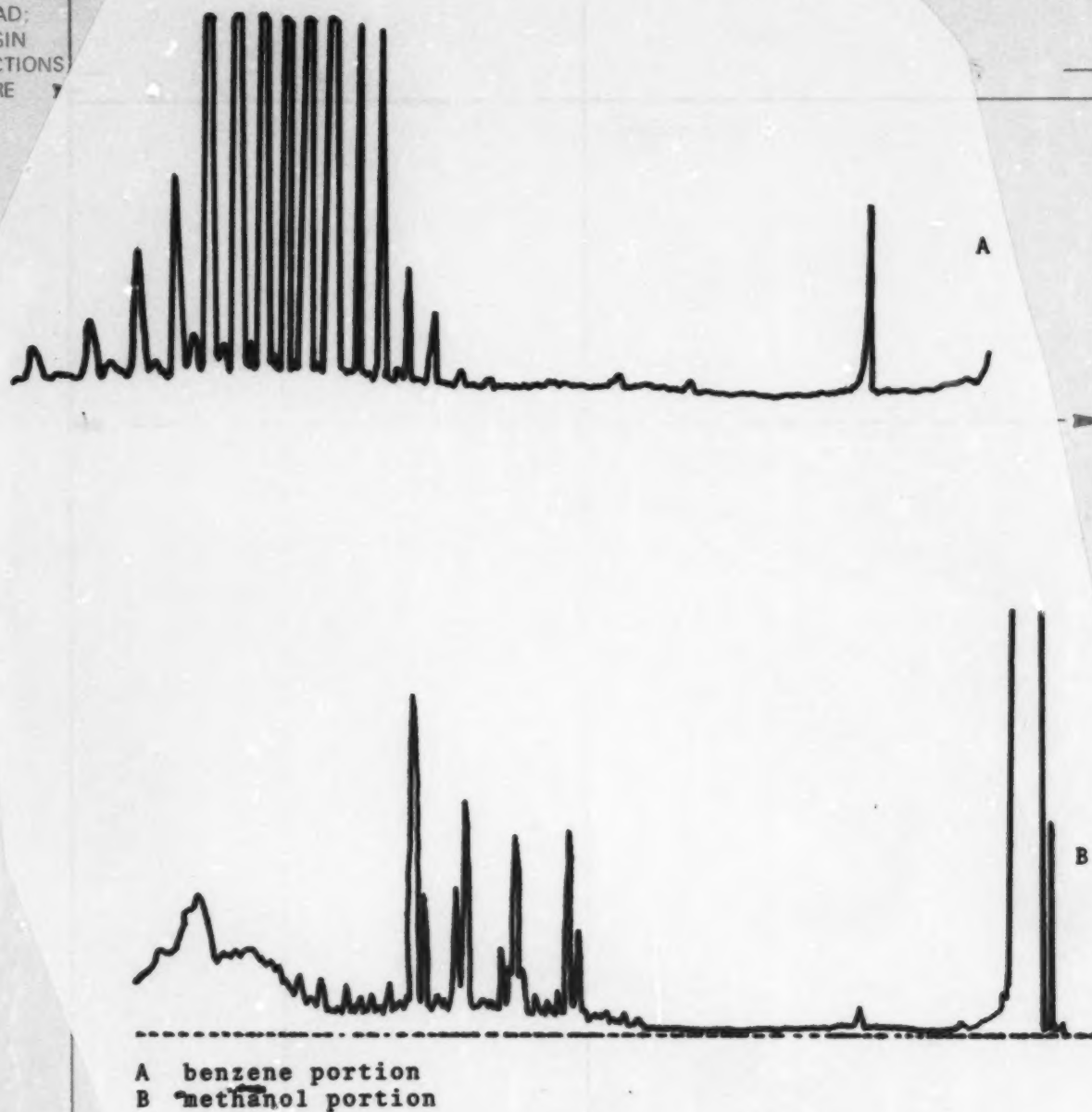
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Figure 24. Mya II (HPP).

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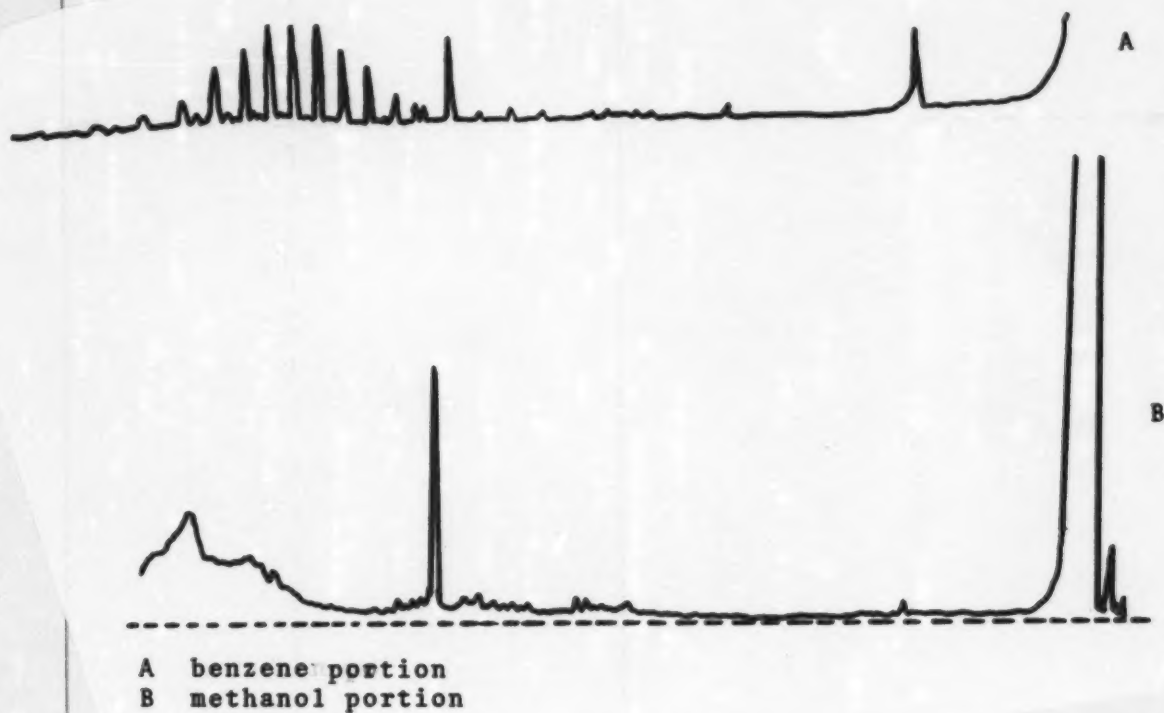


Figure 25. Mya III (LPP).

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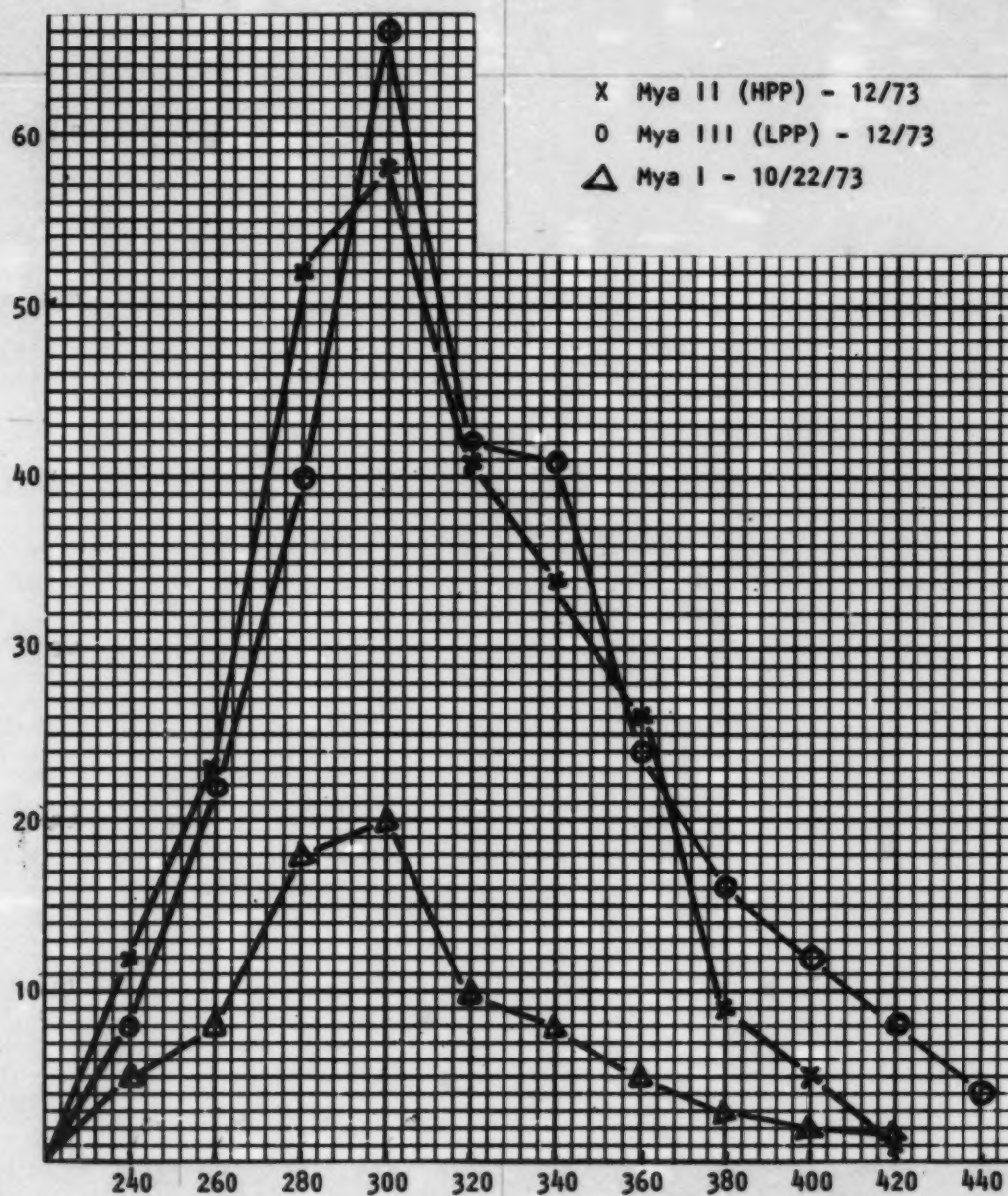
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Figure 26. Maxima profiles for organism extracts.

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SECTION 10

DISCUSSION

It should be stated at the outset that the gas chromatographic methodology that was utilized for this study was not directed toward a routine program of analysis, but rather was directed toward the specific and immediate problem of detection of waste automotive lubricating oils. Any shortening of the life of the chromatographic column by loading with high-boiling materials upon injection was felt to be justified as long as the resolution of resultant chromatograms was not appreciably affected. Any long range, large scale or highly quantitative study could not afford such a luxury.

← The gas chromatograms^{6-1/2"} generated by WCCO and refined petroleum products have been shown to be characteristic and differentiable from chromatograms of other petroleum entities. Weathering appears to have little effect upon some of the specific detection parameters for waste crankcase oils. The continued existence of an unresolved envelope portion, of a number of wide-boiling range compounds, of C₁₇-pristane/C₁₈-phytane peaks, and of a series of n-paraffins above the unresolved portion in chromatographic profiles, together indicate the presence of a specific oil product. All gas chromatograms of sewage effluents and surface waters did not reveal these criteria. Though not conclusive the boiling range of substituents separated and the unresolved portions of the sample chromatograms seem to indicate the presence of a waste petroleum product in samples. Further investigation is needed to generate definite gas chromatographic corroboration with standard WCCO chromatograms. Those chromatographic data for sewage effluents and surface waters may be considered at a preliminary level of assessment and a consequence of sample concentration problems. It is hopeful that these problems will be investigated in subsequent work.

Though the specific source of the waste petroleum detected could not be established in this project, sample analyses strongly indicated that the waste petroleum hydrocarbons detected were derived from waste automotive petroleum products. What was detected could not have been attributable to any other petroleum entity since other standard oil profiles were clearly differentiable from profiles generated by WCCO. Gas chromatograms generated by WPCF effluents did show a range of hydrocarbon compounds above C₂₀; a characteristic of lubricating oils is that they have very few hydrocarbons boiling below n-eicosane⁸⁷. The chromatographic characteristics of an unresolved envelope portion due to the presence of complex PNA compounds was indicated in all environmental extracts taken.

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It has been illustrated by previous investigators⁸⁸, and in this project that the weathering phenomenon that affects a petroleum product once it enters the environment, have less of an effect upon the less soluble and more persis-

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tant aromatic portions of an oil. Bacterial degradative processes have been shown to preferentially attack straight chain, lower molecular weight components with the higher molecular weight compounds being less affected⁸⁹. These aromatic hydrocarbon portions have been known⁹⁰ to adhere to suspended particles in the water column and settle out into bottom sediments with possible subsequent effects upon benthic populations. Gas chromatograms generated by the organism extracts strongly indicated the presence of aromatic compounds from body tissue. Tentative gas chromatographic-mass spectroscopic identification of sub-fractions derived from organism extracts exhibited the presence of alkyl-substituted benzene structures which are indicative of petroleum contamination.

UV-fluorescence spectroscopic analyses furnished the most conclusive evidence for the presence of petroleum in samples and greatly strengthened the analytical results obtained from gas chromatographic analyses. Emission spectra of all samples studied consistently indicated the existence of PNA compounds which could only be attributable to petroleum pollution. With WCCO's unique fluorescence character and characteristic profiles, its presence in environmental samples was established. Further development is needed for future attempts to demonstrate the presence of oil where the existence of oil is only suspect.

The results presented strongly indicate that hydrocarbons discharged into Jamaica Bay, occurring in the surface waters and ultimately becoming incorporated in biological tissue is of a waste petroleum origin. Whether this oil is from intentional or accidental dumping of WCCO into sewers is still unknown. The unique characteristics of the study area and the fact that the major contribution of fresh water input to the Bay comes from WPCF, provides an indication that the detected hydrocarbons are originating from waste crankcase oils and not from other types of petroleum products. Atmospheric washings and JFK airport operations could contribute significant quantities of hydrocarbons to the water column. Further investigation is needed here and subsequent work should note background levels of atmospheric derived hydrocarbons entering Bay waters.

Though the detection of waste petroleum hydrocarbons in the marine environment was a major concern in this project, my ultimate regard lies within the biological significance of this addition to the marine ecosystem. It has been suggested⁹¹ that at least some of the petroleum hydrocarbons retained by an aquatic organism would be an obvious advantage. It could be a means to prevent a loss of equilibration of important biogenic hydrocarbons. On the other hand, recent data indicates⁹² that some marine mussels do not metabolize the hydrocarbons taken up but retain significant amounts in their tissues. These aromatic compounds have been shown not to be found in the environment naturally and would almost exclusively be from a petroleum origin⁹³.

In addition to the known toxicity of such aromatic compounds as benzene and its alkyl-substituted derivatives⁹⁴, specific PNA compounds found in oil waste products have been shown^{95, 96} to be potent carcinogens. Detection of PNA's by UV-fluorescence spectroscopic techniques used in this study and by other investigators⁹⁷⁻⁹⁹ were based upon the stability of these aromatics in the environment and their ability to fluoresce. Detection of such potent and ubiquitous PNA compounds as 3,4-benzopyrene have been exhibited at various

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levels in a variety of marine organisms¹⁰⁰⁻¹⁰³. Investigation into the quantities of such PNA compounds in this environment are needed.

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Recent observations¹⁰⁴ exhibited before a meeting of the National Institute of Environmental Health Services in Washington, D.C. by scientists of the National Marine Water Quality Laboratory in Narragansett, R.I., revealed a high incidence of histopathological effects such as malignant neoplastic growths and cardiovascular abnormalities in marine organisms exposed to petroleum hydrocarbons.

Physiological responses of marine organisms have been shown to be affected by the presence of aromatic compounds in the marine environment. It has been suggested¹⁰⁵ that microscopic chemoreceptors in bivalves will detect the presence of these substances and bring about changes in their filtration rate. The effects on feeding rates, growth rates and reproductive processes should be investigated. The ultimate here being the possible impacts upon marine food chains. Fish and other organisms taken from areas with a history of oil contamination have been found to exhibit elevated levels of compounds which "bioactivate" complex aromatic compounds found in waste crankcase oils, into mutagens¹⁰⁶. The possible long-term adverse effects on the health of human consumers of fish requires greater scrutiny in light of this potential mutagenic burden.

Therefore, gas chromatography, UV-fluorescence spectroscopy and gas chromatography-mass spectroscopy in combination have collectively aided in the detection of petroleum derived hydrocarbons attributable to WCCO in waste water effluents entering the marine environment. The composition of extracted hydrocarbons from a marine organism, especially the content of a series of wide boiling range aromatic compounds, strongly indicates that these samples were polluted by petroleum. The continued addition and existence of these petroleum wastes can only lead to a further deterioration of this marine ecosystem.

Assuming a basis has been established by the results of this project of a large hydrocarbon burden in Jamaica Bay, further steps should be taken in the research of this ecosystem. A total community response to chronic petroleum derived hydrocarbon input should be undertaken. Our coastal areas provide food and shelter for a wide variety of wildlife, both indigenous and migratory. Many commercially valuable fish mature in our estuarine areas. This provides critical support to marine food chains reaching all the way to man. The effects of hydrocarbons on physiology, population dynamics and functions of marine organisms within these wetlands, as well as the public health aspects of chronic hydrocarbon pollution to this area, have yet to be explored.

Finally, Jamaica Bay is one of the few natural resources that remain in the New York metropolitan area. The immediate problems in aquatic pollution that confront these wetlands will be magnified in the future. Even with the Bay's inclusion in the Gateway National Recreation Area, it will be no protection against added pollution. New housing developments, airport operations, offshore oil drilling and deep water ports all threaten the possible irreversible burden of increased hazardous chemicals to this ecosystem. An in-

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creased effort should be aimed at restoring these local waters to the point where they may support a much greater variety of marine life. The idea of fostering a shell-fishery in Jamaica Bay should not be unimaginable.

It is hopeful that this project can initiate an awareness of the increasing quantities of waste oil discharging into our coastal waters through treated and untreated municipal wastewaters and storm sewers. Further investigation and consideration is necessary to understand the overall impact of our urban centers on the environment.

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APPENDIX A

GC BACKGROUND AND THEORY

As an analytical tool, gas chromatographic effectiveness relies for the most part upon the type and construction of the column utilized. In the analysis of petroleum products, it becomes particularly important to know the restraint that such compounds may impose upon a column due to their extensively wide range of high boiling polar and non-polar substances. The type of column utilized in this study was of the open tubular variety where the absorbant is disposed in a thin film or layer on the inner wall, leaving an open, unrestricted path through the column for carrier gas flow. The superiority of open tubular columns for the analysis of a wide boiling range sample mixture in which closely related isomers and homologs are present, has been clearly demonstrated^{1,2}. The use of³⁻⁶ capillary columns for analysis of complex mixtures is also well documented. In addition, the use of open tubular capillary columns for the analysis of such wide boiling range substances from poly-substituted aromatic homologs of benzene and naphthalene⁷, to light petroleum oil products⁸, have produced superior chromatographic results.

The particular type of open tubular column utilized is a SCOT 50 foot x 0.02 inch ID capillary column, coated with the non-polar silicone oil OV-101. This column was used with particular success by scientists at the Woods Hole Oceanographic Institute⁹ for the passive identification of a variety of crude and processed petroleum products.

The use of an ionization detector with the open tubular capillary column has been substantiated¹⁰. Flame ionization detectors (FID) are detecting devices which produce a current proportional to the number of ions or electrons formed upon combustion of sample molecules. Hydrogen and oxygen gases mix at the detector, and are ignited to produce a small flame. As the effluent enters the burner base and mixes with the gases the flame induces ionizations of all organic compounds, with its greatest responses to hydrocarbons.

GC Operating Procedures

Set-up and check-out procedures for the Perkin-Elmer 900 GC

Column

50 ft. x 0.02 in. stainless steel SCOT OV-101 Capillary Column

Injector

Temperature set at $250^{\circ}\text{C} + 10^{\circ}\text{C}$; use of silicone septum suggested

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Carrier Gas

Nitrogen; flow at 4 ml/min measured at column outlet

Oven

*Temperature programmed from 75°C to 300°C at 6°C/min with isothermal operation at 300°C for a minimum of 12 minutes or until chromatogram returns to baseline

Detector

Flame Ionization Detector (FID): manifold temperature set at 300°C + 10°C. Compressed air at 40 psi. Hydrogen at 22 psi. Sensitivity 1×10^{-10} amps/mv

Injections

0.5 to 5.0 ul injections of sample solutions by Hamilton 10 ul syringe depending upon concentrations (split ratio 15:1 installed with a capillary splitter)

Recorder

1 mv, 0.5 in. span; 1 second response; operated at 0.5 in/min chart speed with response positive left to right

* Temperature program dial was calibrated periodically to monitor proper increase in temperature.

Chromatograph are indicated in the operating manual. Unless indicated to be otherwise, all parameters indicated for operation of the gas chromatographic analyses were adhered to for all samples in this study so that visual comparison could be made.

The SCOT column was pre-conditioned at 160°C by Perkin-Elmer Co., however, due to the higher operating temperatures utilized in this study, further conditioning was required. The following is an outline of the column conditioning operation*:

Nitrogen carrier gas flow through column at 4 ml/min

- (1) 220°C for 2 hours
- (2) 250°C for 2 hours
- (3) Four injections standard No. 2 fuel oil; temperature program 75°C-250°C at 6°C/min
- (4) 225°C for 20 hours
- (5) 250°C for 30 minutes
- (6) Five injections standard No. 2 fuel oil; temperature program 75°C-250°C at 6°C/min
- (7) 275°C for 3 hours
- (8) 300°C for 1 hour

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(9) Two injections No. 2 fuel oil; temperature program 75°C-275°C at 6°C/min, isothermal operation at 275°C for 12 minutes

(10) Two injection standard WCCO in petroleum ether (2:1 dilution) temperature program 75°C-300°C at 6°C/min, isothermal operation at 300°C for 24 minutes

* During this entire operation, the column should be disconnected from the detector and a plug placed into the detector inlet port.

The recommended operating range on the SCOT capillary column was no greater than 250°C, however with the high boiling points of the compounds, the operating temperature range for analysis was extended to 300°C. No glass liner in the injector port was utilized as a clean-up procedure and only during the analysis of marine organism extracts was there any sample fractionization performed. Special care was taken to utilize the capillary splitter for standard sample runs. In addition, a "bake-out" procedure (with column not attached to the detector) was conducted after an analysis period to remove high boiling components that may have accumulated on the column.

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The practical sample capacity per injection using a capillary splitter is usually in the order of 10^{-3} ul for the frequently utilized 0.01 inch I.D. (.25 mm) open tubular columns. It has been demonstrated¹¹ however, that by doubling the diameter of the column used, a direct sample injection without use of splitter may be possible. Some overloading of the column was experienced and was alleviated by reducing the injection volume on subsequent runs.

After each conditioning period, as a precaution it would be advisable to run a program sequence to assure that there is no sign of excessive bleed from the column and to establish a baseline. Subtraction of baseline from a chromatographic signal response indicates the unresolved portions in sample profiles.

Analyses of a No. 2 fuel oil or the C₆-C₃₆ standards several times consecutively can serve as a check on procedure and the working conditions of the gas chromatographic system so that any fouling or increases in variability in chromatograms will be detected. A temperature program run without injecting any sample to observe the extent of column contamination or bleeding characteristics after a series of injections is also a good check on system performance, and should be conducted periodically.

Since the cold column (75°C at the start of the program) is attached to a hot injector, many high boilers are trapped on the columns front-end and may accumulate in sufficient quantities to cause septum bleed or exhibit "memory effects" on the next program. These "memory effects" could be attributable to poor syringe technique, contaminated gases entering the instrument, improper maintenance, or the build-up of residues on the septum¹². As a standard procedure, the septum was changed after a set of 10 to 12 injections. To eliminate the problem of "memory effects" a bake-out procedure was again performed after periods of disuse by heating the oven to 300°C for 24 minutes, cooling to 75°C and then programming to 300°C at 6°C/min. The baseline was observed for any contamination on the column.

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UV-Fluorescence Spectroscopy Background and Theory

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Fluorescence spectroscopy as an analytical tool has found extensive use in a variety of clinical and research projects. Its original application had been directed at such diversified studies as the structural state of proteins¹³, as well as the characterization of specific petrochemical products^{14,15}. Recent investigations¹⁶ have exhibited the technique's ability to detect trace quantities of petroleum derived products in oceanic waters.

The theory of fluorometric analysis is that energy absorbed by molecules cause them to move to a condition of higher energy or what has been termed an "excited state". The particular wavelength of radiation (light quantum) emitted by these excited molecules is specific for their particular electronic characteristics. This quantity of light emitted in the fluorescence process is usually of a lower energy than the amount absorbed by the molecule. Therefore, the corresponding loss of energy by a molecule upon returning from the excited state to the ground state becomes the characterizing fluorescence for the molecular species under investigation. The uniqueness of UV-fluorescence analysis is that by exciting any two fluorescing compounds at a specific excitation frequency, unique emission profiles for those compounds will be produced. It is the use of these profiles along with their correlation with standard profiles that determines whether or not a particular class of compounds exists in an environmental sample.

It has been noted that some radiation-free processes occur where molecules return to their ground state after being excited without the emission of a photon, converting all the excitation energy into heat. Little is understood of this process, and due to the inherent inefficiency of this "internal conversion" process, it is believed¹⁷ to be responsible for a relatively small portion of the total excitation energy in most molecules. It is believed¹⁸ that this radiationless process does not exist in aromatic hydrocarbons and therefore should not interfere with analyses.

Fluorescence spectroscopic instrumentation is usually characterized by the use of two monochromators functioning independently of each other. The fluorescence process first requires that energy at a particular wavelength excite a molecule by some external source (excitation monochromator). In the case of the MPF-3 UV-fluorescence spectrophotometer (Perkins-Elmer Co., Norwalk, Conn.) this is accomplished by a 150 Watt Xenon arc. The excited sample, with emission of light at a long wavelength, is now the source of emitted energy for the emission monochromator. The MPF-3 has independent monochromators that may be used to produce from a sample, both emission and excitation frequency on the excitation monochromator and then scanning a range of emission wavelengths, the emission spectrum of the sample may be recorded. It is also possible to excite a particular sample at all possible excitation frequencies while manually scanning the emissions at each of these particular excitation wavelengths. Both of these techniques were utilized in the fluorescence phase of this study.

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Light from the sample is emitted in all directions. The optical set-up of the emission monochromator is usually arranged to take fluorescence from the sample at an angle other than 180° in relation to the exciting light. The

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density of the sample being analyzed dictates the angle at which the incident light will be measured (Figure A1). For example, the low density solution, analyzed in this study, required fluorescence radiation from the sample to be emitted at 90° relative to the exciting light. At higher densities, such as with highly viscous or turbid samples, an angle of 45° or less may be used.

Due to the unique selectivity (especially for compounds with aromatic ring structures) and high sensitivity, fluorescence spectroscopy has been utilized as an analytical technique for samples with concentrations ranging from nanograms to milligrams per milliliter¹⁹.

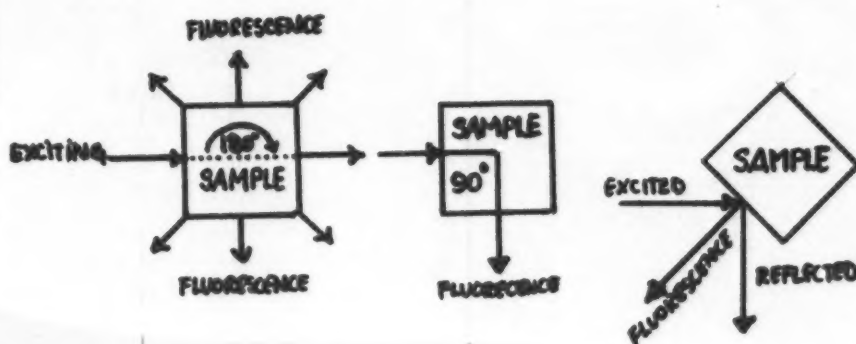


Figure A1.

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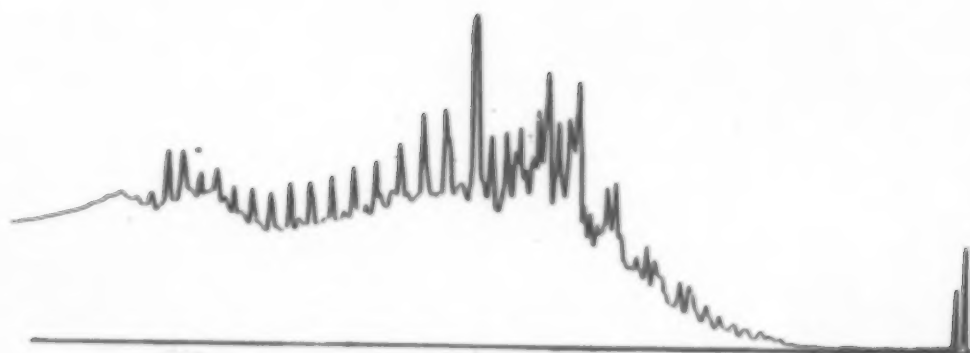
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Bachaquero Crude

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South Louisiana Crude

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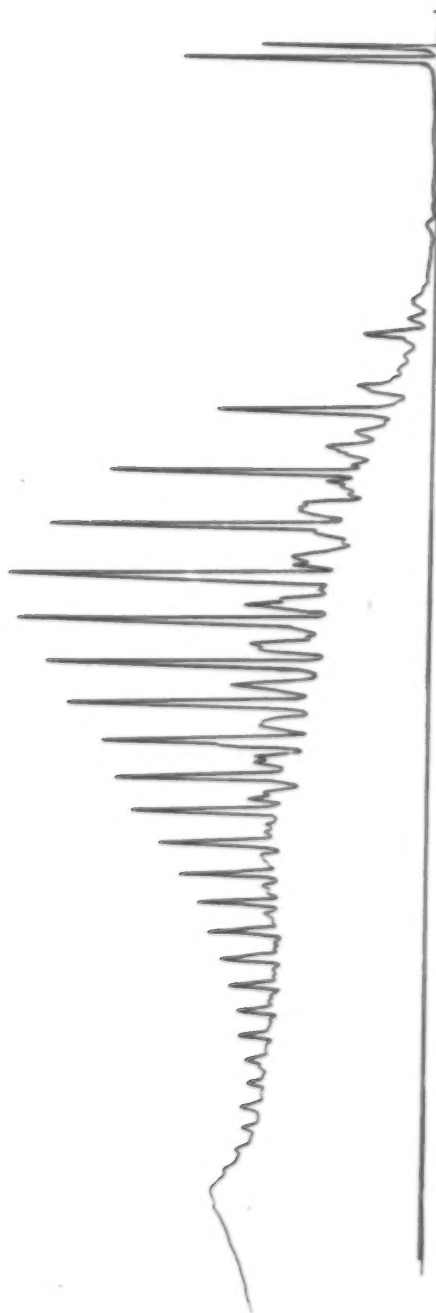
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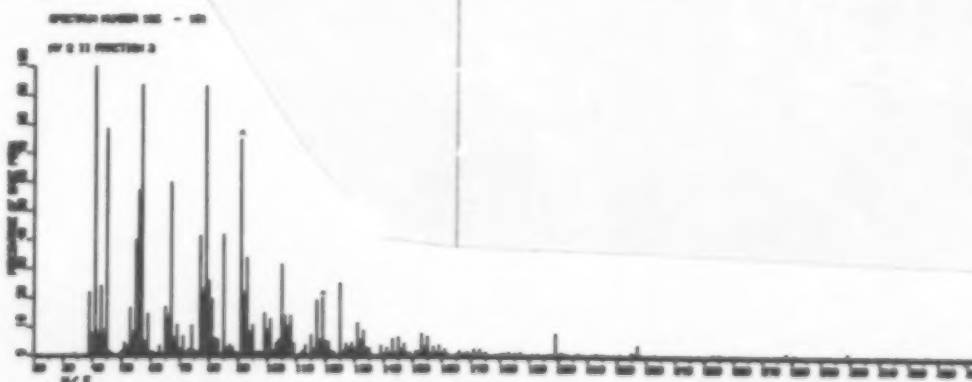
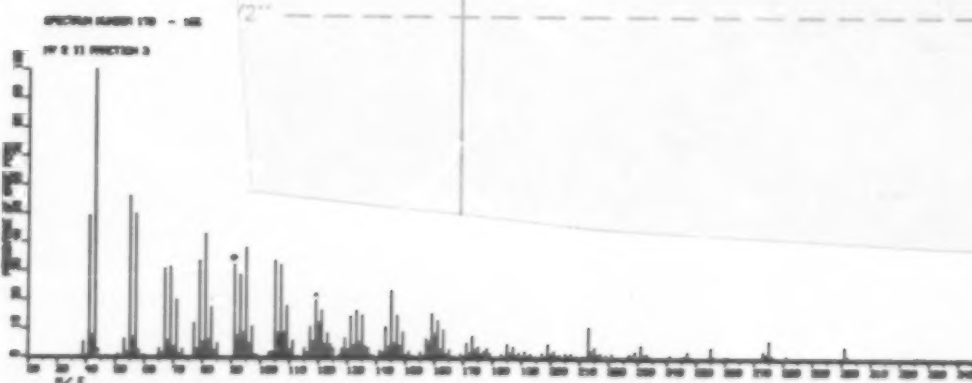
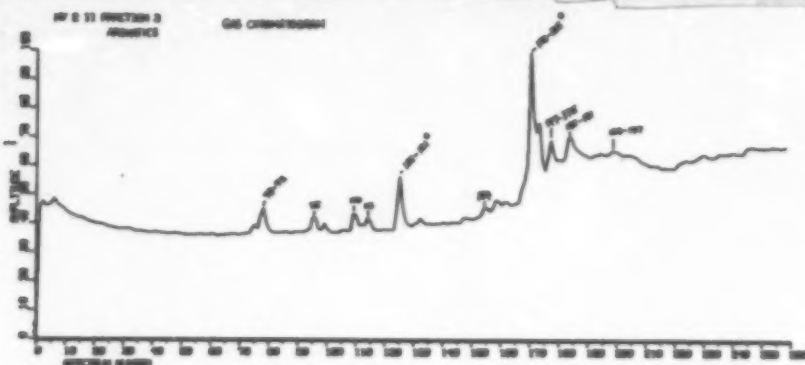
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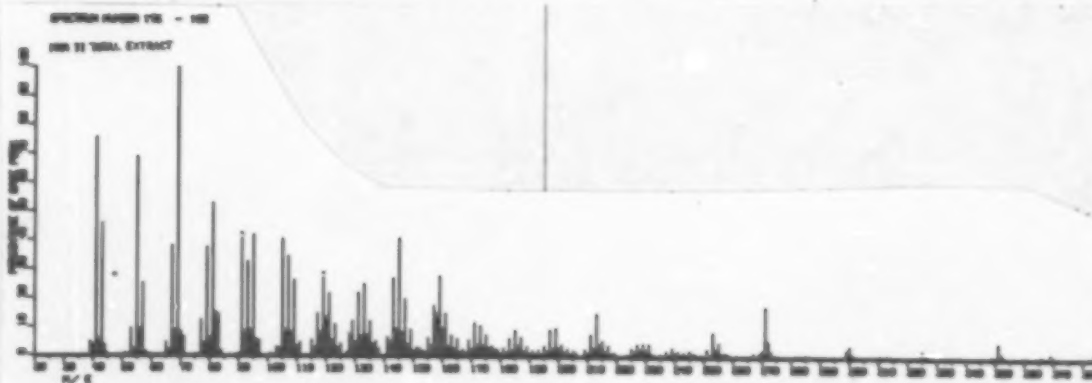
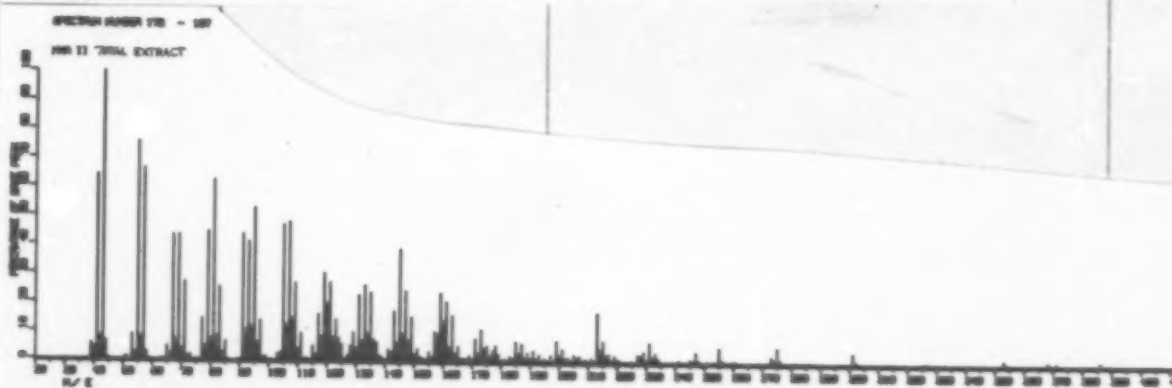
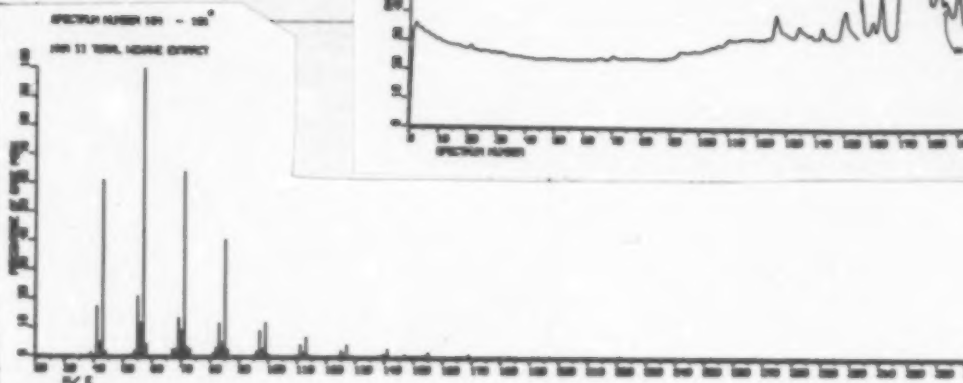
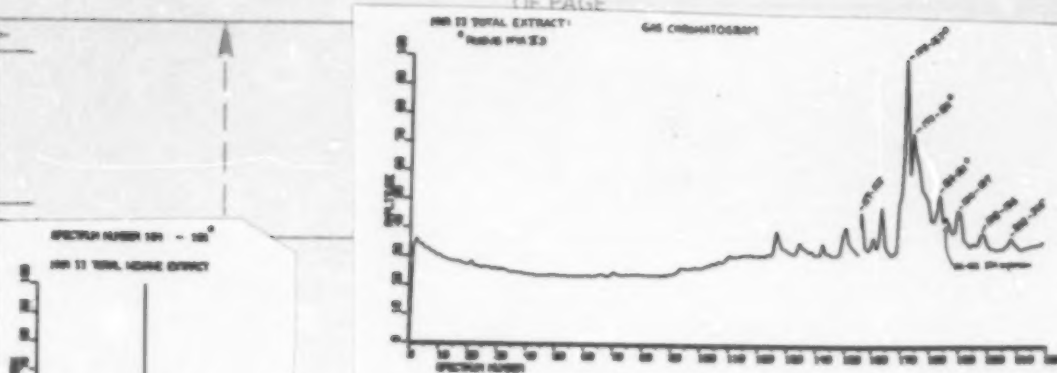
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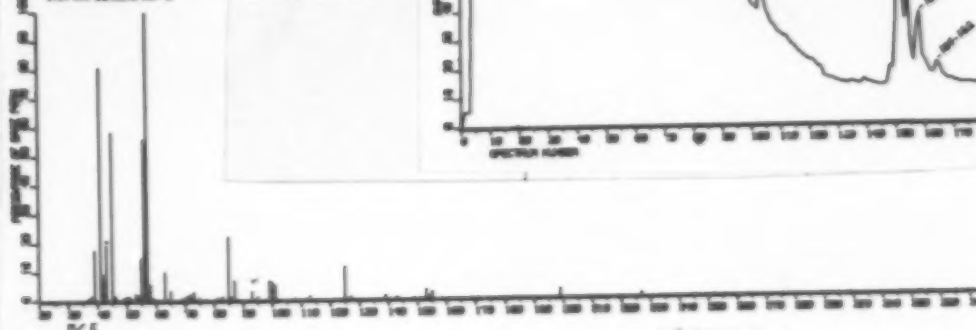
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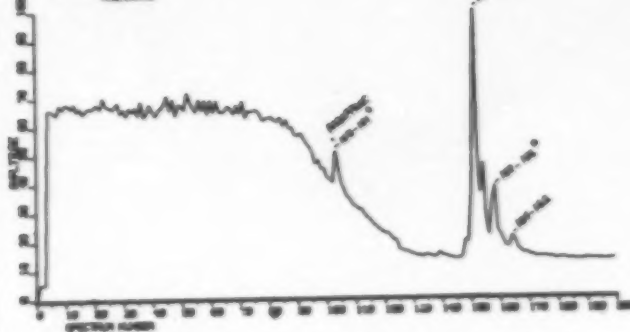
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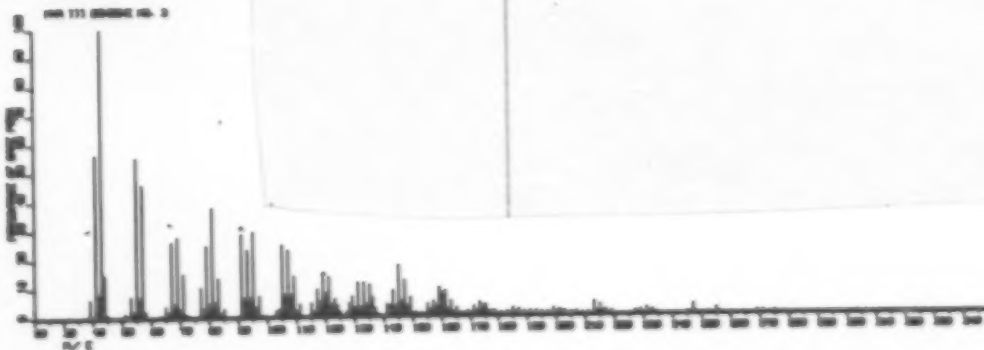


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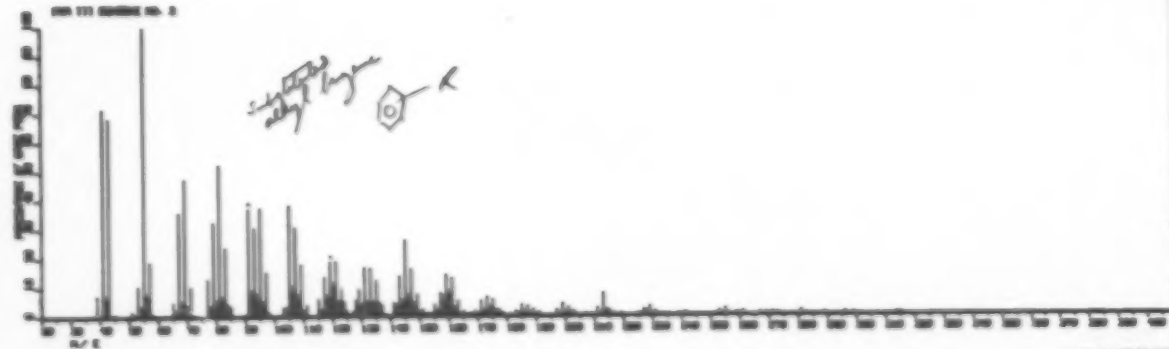
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